University of Alberta

Properties of Water-Bitumen Interface

by

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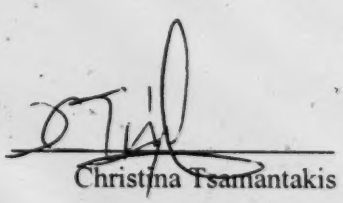

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Dedication

Με απέραντη αγάπη στην αδερφή μου Μαριάννα.

I happily dedicate this thesis to my beloved sister, Marianna. Her encouragement and emotional support during the past two years are greatly appreciated.

Στους γονείς μου που, με τον τρόπο τους, μου συμπαραστέκονται και με αγαπάνε.

To my parents, for always being supportive of me.

Abstract

Micropipette techniques were used to directly explore the in-situ behaviour of single emulsion drops. The size of the drops is that typically found in a commercial oil sands operation. All experiments were conducted using an optical microscope. Two different emulsion systems, which are formed during oil sands processing, were investigated.

Initially, interfacial tension measurements and rigidity tests were conducted for water-in-diluted bitumen systems. In general, the interfacial tension on the water droplet surface decreased as bitumen concentration increased. Different solvent mixtures had little effect on the interfacial tension. Furthermore, crumpling of the interface was influenced by bitumen concentration, type of solvent and water pH.

Subsequently, bitumen-in-water emulsions were studied. Bitumen drops were individually stretched in de-ionized water in the presence of montmorillonite clays and/or calcium ions. In general, the surface plasticity of bitumen drops is enhanced when increasing both calcium ion concentration and temperature.

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List of Symbols

Γ	Molecular surface coverage (m^{-2})
σ , γ	Interfacial tension (N/m)
B_o	Bond number, $B_o=\Delta\rho R_d^2/\gamma$ (-)
C_o	Volume percentage of bitumen in the oil phase (% vol.)
g	Gravitational acceleration (m/s^2)
k	Boltzmann constant, $k=1.381x10^{-23}$ J/K
L	Axial drop length (m)
n	Number of terms in series solution (equations 3.1, 3.2, 3.3 and 3.4)
N_p	Fraction of bitumen drops that behave plastically
P	Pressure field (Pa)
P_{cr}	Critical pressure (Pa)
R	Cylindrical coordinates (m)
R_1	Merdional radius of curvature (in s direction) (m)
R_2	Azimuthal radius of curvature (about z axis) (m)
R_d	Spherical drop radius (m)
s	Curvilinear distance along drop surface, from z=0 (m)
t	Time (s)
T	Temperature (K, °C)
x	Linear coordinate (m)
y	Linear coordinate (m)
z	Cylindrical coordinate (m)
ρ	Density (kg/m^3)

List of Abbreviations

DIW	De-ionized water
DRU	Diluent recovery unit
heptol[A]	Mixture of toluene and heptane with the volume percent of toluene being A
IFT	Interfacial tension
M	Montmorillonite clays
MFT	Mature fine tailings
PSV	Primary separation vessel
PW	Aurora process warm water
SS_E	Sum of squares error
TOR	Tailings oil recovery unit

Chapter 1

1 Introduction

1.1 Emulsions

An emulsion (or macroemulsion) is a dispersion of a liquid in another liquid in which it is immiscible (Hunter, 1993). The dispersed droplets are spherical in shape and often show great polydispersity (Hiemenz and Rajagopalan, 1997). The study of emulsions has reference to engineering, agriculture, biology and medicine (Hunter, 1986).

Emulsions are two-phase systems and, because of the free energy associated with the interface, they are thermodynamically unstable with respect to separation into two phases. Any two immiscible liquids can be made to form emulsion droplets under appropriate conditions, but a stable emulsion will only result if the reverse process of coalescence and phase separation is sufficiently slow. It is generally necessary to introduce a third component to stabilize the emulsion by adsorbing at the interface between the two liquid phases. Such a component is often called a stabilizing agent. Such an agent is also referred to as an emulsifier. The most common emulsifiers are macromolecular stabilizers (like proteins, polysaccharides) and surfactants. A surfactant molecule consists of two parts with very different characteristics: one part is polar, a dipole or a charged group, and the other is non-polar, e.g. a hydrocarbon chain. Due to the fact that each part has very different solubility properties with water, the surfactant molecules tend to accumulate at the interface with the polar part locating itself into the polar phase and the non-polar part being in the hydrocarbon phase (Hunter, 1993). Adsorption of these stabilizing agents on an interface alters the surface properties of the

emulsion drop surfaces and, as such, it may change the overall mechanical behaviour of the emulsion drops.

The most fundamental surface property of any liquid-liquid interface is the interfacial tension. Interfacial tension refers to the energy required to create a unit of interfacial area between two immiscible liquids. When surfactants are present in the emulsion and adsorb at the interface, the interfacial tension is lowered. The pressure across a curved interface is related to the interfacial tension by the Young-Laplace equation (1805) according to:

$$\Delta P = \sigma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \qquad (1.1)$$

This equation describes curved interfaces, which in this case, are those of the emulsion drops. ΔP is the pressure difference across an arbitrary curved interface and σ is the interfacial tension. The term in the parenthesis comprises the mean curvature, where R_1 and R_2 are the principal radii of curvature (Adamson, 1976). When dealing with spherical drops, the mean curvature is simplified to $2/R_d$, where R_d is the drop radius. Furthermore, other surface properties that may influence the mechanical behaviour of emulsion drops are interfacial viscosities (Plateau, 1869; Boussinesq, 1913) and elastic or/and viscoelastic interfacial properties (Evans and Skalak, 1980; Edwards et al., 1991).

To date, most techniques used to study the rheological properties of interfaces are composed of macroscale studies involving a sample size of millimetres or larger (Edwards et al., 1991; Miller et al., 1996). These studies are further enriched with the help of more advanced methods (Wu et al., 1998). Leading up to emulsion droplets, which are micrometer-sized droplets (on the order of 10^{-3} mm), micron-scale studies on emulsions have been limited to the imaging of emulsion structures (Gafonova and Yarranton, 2001; Yarranton et al., 2000).

It has been recently demonstrated that, in the presence of surfactants, the interfacial tension between two immiscible liquids depends strongly on the experimental design (Yeung et al., 1998). It can be presumed that other interfacial properties may be affected by the length scale considered. As a result, it is important to study the micrometer-size emulsion drops at the appropriate length scale. Apart from its advantages for visualization, the micropipette technique has recently been introduced allowing a more direct intervention with the emulsion system (Yeung et al., 1998). This method will be the tool in examining the behaviour of emulsion droplets throughout this research. Oil-water emulsions will be studied. They are widely used in many industrial processes such as paint making, food processing, sizing in paper-making, medicine formulation, road surfacing and oil recovery (Evans and Wennerstrom, 1994).

In particular, the behaviour of crude oil-water interfaces, often encountered in the oil industry, will be the focus of this study.

1.2 Brief review of previous studies on oil-water interfaces

"By and large, crude oils and bitumen contain suspended fine solids, asphaltenes, resins, saturates and aromatics. The proportion of these species is very much dependent on the type of crude oil and bitumen's origin" (Yan et al., 1999). The above statement simply emphasizes the fact that the overall behaviour and characteristics of various crude oils and bitumen samples will differ appreciably as a result of their origin or even the way they have been treated. Because coker feed bitumen extracted from Athabasca oil sands is considered in this study, special interest will be given initially to its characteristics and behaviour. This will be followed by a short reference to studies that describe bitumen having the same origin as those described here (Athabasca). A quick reference to general studies on oil-water interfaces is given below.

Bartell and Neiderhauser (1949) observed the formation of a "solid" film at the crude oil-water interface of a pendent drop. In order to further investigate the formation of these films they isolated them and observed that the films were highly surface active and asphaltic in character. They also noticed that solid film formation was accompanied by the lowering of interfacial tension, and thus concluded that these films were formed by an adsorption process. However, since the film forming material was strongly adsorbed by solid surfaces, it was believed that it would not be present in crude oils as the oils exist in their natural subsurface reservoirs. Later, Reisberg and Doscher (1956) using rigorously controlled anaerobic conditions during crude sampling as well as during laboratory measurements, eliminated the possibility that rigid film formation was only due to atmospheric contamination. While changing the pH of the aqueous phase, they noted that at a pH above 8, rigid film formation became negligible. A few years later, Dodd (1960), in order to gain more insights on the reason(s) for "skin" formation, measured the rheological properties at oil-water interfaces by developing an interfacial film viscometer. Kimbler et al. (1966) used a modified Langmuir balance to study the compressibility and collapse pressure of the interfacial films occurring between certain crude oils and water. In 1968, Strassner (1968) used the pendent drop technique to further investigate the film-forming material(s) present in a crude-brine system. He stated that interfacial films, when retracted, exhibited one of three different physical behaviours. Depending on the quantity of asphaltenes and resins in a crude oil, which are believed to primarily stabilize the oilfield emulsions, these compressed films have rigid, soap-type or minimum film properties. In addition, Strassner (1968) found that pH and composition of the brine strongly affected emulsion stability. Neustadter et al. (1975) approached the concept of interfacial rigidity from a different viewpoint by stating that the stability of water-in-crude oil emulsions is mostly attributed to the adsorption of natural surfactants existing in the crude oil on the water-crude oil interface. As a consequence of this adsorption mechanism, the properties of the resulting interfacial film can be alternated (e.g. its viscosity and elasticity). In a later investigation by Brown et al. (1977), again, interfacial

skin was produced by reduction in the extent of a crude oil-water interface. In the above study, oil-water interfacial shear viscosity and pseudo-static compressibility were used to describe water-in-crude oil emulsion stability. Destabilization of such an emulsion is attempted by adding chemical demulsifiers and examining their influence on interfacial film compressibility. Film displacement and film inhibition are the two mechanisms of chemical demulsification that are identified here. In two subsequent studies by Jones et al. (1978) and by Neustadter et al. (1981), modification of the interfacial properties, such as interfacial tension, interfacial shear viscosity and interfacial film compressibility resulting from the addition of chemical demulsifiers, is discussed. More recently, Pasquarelli and Wasan (1981) fractionated a California crude oil using vacuum distillation. They attempted to examine the subsequent changes on naturally occurring film formed at the crude oil-aqueous interfaces. Measurements of interfacial charge, interfacial tension and interfacial viscosity were conducted in order to explain the gradual changes in the structure of the interfacial films. Again, it is noted that the heavy asphaltic components in crude oils are primarily responsible for the high interfacial activity and hence, the resulting dynamic interfacial properties. Mohammed et al. (1993) measured the rheological properties of the interfaces formed between a Buchan crude oil and water using a biconical bob rheometer. Temperature effects and the presence of demulsifiers were also recorded. Kim et al. (1995) also conducted dynamic film tension measurements, film stress-relaxation measurements, drop volume measurements of interfacial tension and adsorption kinetics measurements on a water-oil-water film.

1.3 Oil sands

Gas and oil have greatly attributed to industrial development in the 20th century. However, the easily exploitable conventional oil reserves are depleting throughout the world. The same is true for Canada which luckily, up to now, has been self-

sufficient in oil production. Canada's energy supply is enhanced by the huge oil sand deposits in northern Alberta. Typically, the oil sand ore consists of about 6-13 wt % bitumen. The total amount of bitumen in Alberta, including bitumen from oil sands, is estimated at 1.3 trillion barrels (Outtrim and Evans, 1977). As a result, if oil sands production is further developed, the country's energy supply is expected to be assured for at least one more century.

The world's largest known oil sands deposit is located in the Athabasca region, north eastern Alberta. About 15% of Canadian oil consumption comes from the Athabasca oil sands (Czarnecki, 2001). In this area, the ore is located close to the surface, allowing for surface mining. In general, only 15% of Alberta's bitumen is considered surface-mineable. Oil sands are unconsolidated sands deposits consisting of high molar mass viscous petroleum. This is better known as bitumen. The chemical structure of bitumen is similar to that of conventional oil but bitumen has a higher density and viscosity. Oil sands contain roughly 82% by weight minerals and what remains is distributed between bitumen and water. The ore is characterized as rich, moderate or lean depending on the bitumen concentration. When the bitumen content is more than 10% by weight, the ore is considered rich, while an ore with bitumen content between 6 to 10% by weight is regarded as one of moderate quality. Finally, less than 6% by weight bitumen is considered a lean ore (Takamura, 1985).

After the ore is mined and crushed, it is mixed with water and pumped to the extraction plant (Figure 1.1). This is accomplished by a hydrotransport pipeline system, which is a new technology that is implemented recently. The slurry temperature in the pipeline is about 50°C and, at that point the ore is digested and the bitumen is liberated. Additional air is introduced in the pipeline and as a consequence, the formed air bubbles attach to the liberated bitumen droplets.

The slurry is then fed to a gravity settling vessel, called "primary separation vessel" (PSV), where the aerated bitumen floats to the surface forming a froth. It

is necessary to prevent solids build up, thus a stream is retrieved from the middle of the PSV, known as "middlings". This stream contains a small amount of poorly aerated bitumen droplets that are not able to float to the surface and most of the fines. The bottom stream from the PSV, called the "primary tailings", contains coarse solids and residual bitumen. Next, the middlings and primary tailings streams are combined in order to be treated further. The continued stream is sent to a tailings oil recovery (TOR) unit and to flotation cells.

The combined froth from the PSV and flotation cells contains roughly 60% bitumen, 30% water and 10% solids (Shaw et al., 1996). Further treatment of this froth includes the removal of solids and water. This is done with the help of centrifuges and inclined plate settlers in the froth treatment process. For that purpose, the addition of a light solvent (locally produced naphtha) is necessary during the froth treatment. In this way, the density and viscosity of the oil phase are reduced, making water and solids separation possible. The product after froth treatment usually contains about 2% water and 0.4% fine solids and is ready for upgrading (Masliyah, 2000). At that stage, the diluent is recovered at the diluent recovery unit (DRU) and recycled to froth treatment. In total, more than 90% of the bitumen contained in the oil sands is recovered.

Finally, the bottom streams from the flotation processes, apart from containing mostly solids and water, also contain about 2% of emulsified bitumen. These streams are called tailings and are sent to a tailings pond where the solids are allowed to settle. It has been reported that roughly one million cubic metres of tailings are discharged into a tailings pond daily (Kasongo et al., 2000). The purpose of the above tailings treatment is the consolidation of the fines to a sediment, which is called mature fine tailings (MFT). This process normally requires several years. Further consolidation of the MFT in order to be transformed to a productive soil layer would require hundreds of years. Based on the above, a new tailings management scheme was developed to reduce the areas for tailing disposal by fast release of water for recycle to the extraction plant. This

process is called consolidate or composite tailings (CT) and is based on gypsum addition [$CaSO_4 \cdot 2(H_2O)$] as a means to achieve fast settling of the fine tails in order to produce water for processing freshly mined oil sands. According to Lord (1998), the combination of about 1 kg/m^3 of gypsum with MFT accelerated the consolidation of the MFT. After 30 days, a consolidated sentiment, which acts like solid earth, was formed with a solid content as high as 82% by weight (Masliyah, 2000). The use of gypsum seems to be the key component for fine tails treatment: the addition of Ca^{++} causes the fines (clays) to aggregate and the addition of coarse solids acts as an extra load on the aggregated clays.

1.4 Problem definition

As mentioned earlier, the bitumen product leaving the last centrifuge (point A in Figure 1.1) still contains 2 to 3% water and 0.4% solid particles (Shaw et al., 1996). The problem is that the residual water contains chlorides, which are then carried through the froth treatment product stream to the upgrading operations, creating corrosion problems. Chlorides, which mainly come from the ore, accumulate in the process water because of water recycle. The residual water (~2%) is dispersed in the diluted bitumen in the form of small (i.e. of the order 1-10μm diameter) stable water droplets. It is interesting to note that these water droplets have been identified even at an earlier stage in the process, when they are still part of the froth (Mikula, 1992). Optical microscopy, previously used in emulsion characterization, revealed that froth product contains small but stable water droplets dispersed in bitumen (Chung et al., 1991). Removal of this emulsified water with conventional techniques has not been very successful as yet. When the excess of chloride salts contained in this water is treated with hydrogen at hydrotreatment, hydrochloric acid results as a product. This, combined with the fact that organic nitrogen is converted into ammonia, creates the ideal conditions for the formation of volatile ammonium chloride (Czarnecki,

2001). Therefore, the removal of the stable emulsified water in diluted bitumen is imperative.

Yet another important issue here has to do with the addition of gypsum in the consolidated or composite tailings (CT) process. The use of gypsum is beneficial in reducing the areas for tailings disposal by rapid release of water. The released water is recycled back to the extraction plant for processing a freshly mined ore. However, the use of gypsum in the CT process increases the concentration of calcium and other ions in the recycle water. The negative effect of these ions on oil sands processibility is well-documented (Sanford and Seyer, 1979; Sanford, 1983; Smith and Schramm, 1992). On the other hand, bitumen recovery is directly related to the ore quality. That means, low-grade ores give lower bitumen recovery. This characteristic is associated with the high fines and high connate water content (i.e. high salt content) in the low-grade ores. Overall, the combined high calcium and associated ions concentration in the recycle water coming from the tailings pond along with processing a low-grade ore (high in fines and salt concentration) drastically depresses bitumen recovery in the separation vessel (point B in Figure 1.1).

1.5 Specific objectives

The purpose of this thesis is to provide better insights for both problems mentioned in the preceding section. Initially, the rigidity of water in diluted bitumen emulsion was investigated. It has been reported that different diluents (solvents) behave in different ways during froth treatment. As a result, the observed rigidity on the water droplet surfaces will be very much affected by the nature of the solvent used to dilute the bitumen during the froth treatment. Secondly, the formation of bitumen-in-water emulsion will be studied. The purpose is to investigate bitumen droplets behaviour and see how this may be

affecting bitumen recovery. The combined effect of calcium ions together with clay particles on the surface properties of bitumen droplets will be investigated.

More specifically, the objectives of this study are:

1. To test the surface rigidity of water droplets in diluted bitumen by varying the bitumen concentration and the solvent ratio. Hep-tol (a mixture of heptane and toluene) will be as a solvent. Furthermore, the interfacial tension of the above systems will be measured. The surface rigidity of the system of water droplets in diluted bitumen will be tested by varying the pH and the bitumen concentration. This study is further described in Chapter 2 of the thesis.

2. To examine the effects of clays when coexisting with calcium ions in a system of bitumen droplets in water. In addition, the surface behaviour of bitumen drops will be studied at different temperatures. Details are discussed in Chapter 3.

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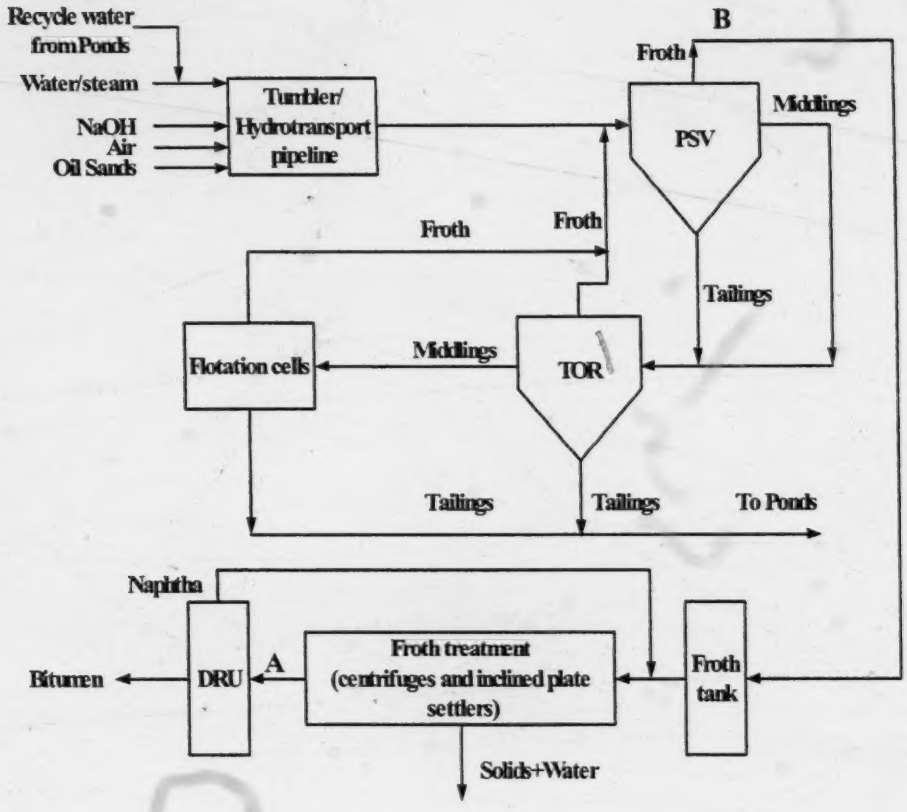

Figure 1.1: Syncrude's bitumen extraction process.

Chapter 2

2 Water-in-diluted bitumen emulsions

2.1 Introduction

To date, the primary research focus of the petroleum industry has been on the elimination of water from water-in-crude oil emulsions. These emulsions are of great interest for two reasons:

- They exist in both bitumen extraction and conventional oil production facilities during extraction or cleaning. The volume of emulsified water increases the total volume of the crude oil. As a consequence, the industry has to deal with larger production volumes, which increase the cost of transportation and refining.
- They form spontaneously in oceanic oil spills. Water-in-crude oil emulsions appear to be very stable and the oil in these emulsions is very difficult to recover, thus increasing the overall problem of environmental damage.

Fingas (1995) presented a review of the physics and modelling of water-in-oil emulsions. However, it is clear that our understanding of the emulsification mechanism is still incomplete. The kinetics and energy of emulsion formation are not well understood. Studies conducted by Environment Canada focus on the physics of emulsion formation (Bobra, 1990; 1991; 1992). Results indicate that emulsion formation is a consequence of surfactant-like behaviour of polar and asphaltene compounds. Both are similar compounds and behave like surfactants.

The majority of investigators believe that asphaltenes, the fraction of crude oil soluble in toluene but insoluble in alkanes (typically pentane or heptane), are

responsible for stabilizing water-crude oil emulsions (Yarranton et al., 2000). Asphaltene monolayers were observed in a Langmuir trough, suggesting that asphaltenes act as surfactants (Nordli et al., 1991). Another research study claims that water-in-crude oil emulsion stability is related to the asphaltene precipitation point (Eley et al., 1988). This observation infers that molecular or colloidal asphaltenes near or at the point of precipitation may stabilize emulsions. In other observations from electron micrographs, fine particles were observed on water-crude oil interfaces, suggesting that particulate asphaltenes stabilize emulsions. Rheological studies also indicate that water-crude oil interfaces contain particles. The accepted theory is that asphaltenes, in colloidal form, stabilize emulsions as a network of cross-linked aggregates. It has been observed that stable emulsions can be formed even at relatively low crude oil concentrations and that the investigation of these emulsions can provide useful insights into the stabilization of water/crude oil emulsions (Yarranton et al., 2000).

When referring to bitumen, which is very similar to conventional crude oil except that it has higher density and viscosity, dilution of the bitumen phase is unavoidable when studying water-in-bitumen emulsions. The following is a short review on studies related to Athabasca extracted bitumen. This bitumen constitutes Syncrude's coker feed bitumen.

Yarranton et al. (2000) studied water-in-hydrocarbon emulsions stabilized by asphaltenes. The asphaltenes were precipitated from bitumen and were divided into soluble and insoluble fractions by dissolving them in a solvent (toluene) and then adding a precipitator (hexane). The stability of water-in-hydrocarbon emulsions was examined by measuring the surface area of these emulsions stabilized by the various asphaltene fractions, each with different proportion of soluble and insoluble asphaltenes. It was concluded that asphaltenes appeared to act as both molecular surfactants and stabilizers of water-in-hydrocarbon emulsions. Only the fraction of asphaltenes that was both soluble and surface-active was found to adsorb on the interface and stabilize the emulsions.

On a macroscopic scale, Yan et al. (1999) studied the ability of various bitumen components to stabilize water-in-hydrocarbon emulsions. Asphaltenes, deasphalted bitumen and fine solids comprised the various bitumen components under investigation. The remarkable stability of water-in-diluted bitumen was attributed to the presence of asphaltenes and fine solids. These two components were able to independently stabilize water-in-diluted bitumen emulsions. It was noticed that solids larger than 8μm do not affect the water-in-diluted bitumen emulsion stability as effectively as smaller solids. On the other hand, without either asphaltenes or fine solids, diluted bitumen on its own did not appear as effective in stabilizing the emulsified water. However, water-bitumen interface was stabilized not only by asphaltene molecules and solids but also by other molecules contained in the deasphalted bitumen.

In a recent study, Gafonova and Yarranton (2001) examined the stabilization of the water/hydrocarbon interfaces by varying additional parameters. The stability of water-in-hydrocarbon emulsions was tested by adding different amounts of asphaltenes, resins and solids. The effect of different hydrocarbon components on the emulsion stability was tested by using various ratios of toluene/heptane mixtures in order to simulate a continuous model oil phase. It was concluded that all three bitumen components played a significant role in the water-in-hydrocarbon emulsions stabilization: native solids and asphaltenes played the role of emulsion stabilizers, while resins destabilized emulsions. In addition, it was found that emulsion stability increased in poor solvents (i.e. heptane). Again, emulsion stability was attributed to solids that were less than 1 μm in diameter.

Another important study reported by Czarnecki (2001) concentrated on the scientific aspect of the issue of water-in-oil emulsion stability. Initially, a newly developed colloidal collider technique was used to study the interactions between micrometer-sized droplets. The stabilization of the emulsified water droplets appeared to be mainly the result of steric repulsion between adsorbed layers on

the droplets surfaces. Electrostatic forces, on the other hand, played a minor role in contributing to steric stabilization. The continuing application of the micropipette technique offers visual observation of this protective rigid "skin". Crumpling of the interface of water droplets is observed at low bitumen concentrations (up to 1% by volume), while crumpling disappears at high bitumen concentrations (~10% by volume). The above concentrations indicate that emulsions of water in diluted bitumen appear to be more stable at low bitumen concentrations with the interface becoming highly flexible as bitumen concentration increases. Also, Czarnecki (2001) reports that the thickness of this interfacial film is also very much dependent on the diluent ratio. Further, it was observed that the film separating two water droplets in heptane-diluted bitumen was about half the thickness when only toluene was used as a solvent.

The micropipette technique, a "tool" exclusively used until recently in the field of biophysics (Evans and Skalak, 1980), was first introduced by Yeung et al. to the oil sands research field. Yeung et al. (1998) initially reported the imperative need to use micropipettes when dealing with emulsion systems (i.e. the dispersed drops are of the order of 10 μm in diameter). The interfacial tension (IFT) of two immiscible fluids was measured using different techniques. It was concluded that in the presence of surfactants, interfacial tension values quantified on a "lab" scale (i.e. involving sample size of millimetres or larger) may vary significantly from the IFT values "deducted" from the surfaces of micrometer-size emulsion drops. Great discrepancies in the IFT value were recorded when the same amount of surfactants occupied vastly different bulk volumes and different interfacial areas. As a result, when dealing with surfactants adsorbing on the surface of micron-size emulsion drops, the appropriate way to quantify this micron-scale surfactants partitioning is by using a micron-scale method to measure the interfacial tension. To conclude, it is necessary to conduct tensiometric studies on the same length scale as the individual emulsion drops.

Following that, Yeung et al. (1999; 2000) systematically observed the surface behaviour of water droplets in diluted bitumen under different conditions. It was aimed at better understanding the reason(s) causing the remarkable stability of water droplets in such emulsions. The stability of water droplets in diluted bitumen was already identified as one major problem that researchers tried to resolve. In the oil sands industry, the term "stability" of water droplets represents the condition of its final product: even after the last centrifuge process and just before the diluent is recovered, the diluted bitumen stream always contains a small amount of water (~2%). Further details regarding the process are given in Chapter 1. The water is dispersed in the diluted bitumen phase in the form of small (on the order of 10 μm) water drops. Yeung et al. (1999; 2000) visualized first this well-known "stability". Using the micropipette technique, the water-in-diluted bitumen emulsion stability was demonstrated in two ways. First, two droplets were forced to interact in 0.1% diluted bitumen (heptol[50] was used as diluent: a 50/50=heptane/toluene solution). Even after 5 minutes of forced contact between them the water droplets did not coalesce; moreover, they remained totally separated entities after force removal. This clearly reveals resistance to coalescence. The second visual observation of stability was obtained when a spherical water droplet was formed by expelling a small amount of water from a water-filled micropipette. The micropipette was again immersed in 0.1% diluted bitumen. As the water content of the drop was then withdrawn via the micropipette, the surface of the water drop crumpled abruptly, revealing a rigid structure, which probably behaved as a steric barrier. No crumpling of the interface was observed when the water droplet was deflated in pure heptol and when no surfactants were present. The droplet always remained spherical throughout the deflation process. The rigidity of the water droplet surface imparts remarkable stability on the interface. In summary, the use of the micropipette technique to study emulsions formed during the oil sands process brought the researcher closer to the concept of emulsion stability, and thus, closer to the problem's solution.

Application of the micropipette technique has been attempted by van der Kloet et al. (2001). The above study concentrated on the effects that surface active components of bitumen froth have on the interfacial properties of various water-in-oil emulsion systems. It was found that, while asphaltenes appear to act as the primary stabilizers of the interface, other froth components were surface active as well and could influence the water-in-oil emulsion stability even upon asphaltenes removal.

To date, most studies on the rheological properties of interfaces of emulsion (or macroemulsion) drops are limited to the use of macroscale studies involving sample sizes of millimetres or larger (Edwards et al., 1991; Miller et al., 1996). Common examples of such techniques are: a) the Du Noüy ring and the Wilhelmy plate, which measure the force to traverse an object through an interface; b) the drop volume method, which is based on balancing the gravity forces against the capillary effects; c) the spinning drop method, which examines drop deformation caused by centripetal acceleration, and d) the pendent and sessile drop methods that are based on the analysis of gravity-deformed drop shapes. Recently, optical microscopy was used to observe the droplets in these emulsions (Gafonova and Yarranton, 2001; Yarranton et al., 2000). With the wavelength of visible light being roughly equal to 0.5 micron, the water droplets formed in the emulsions (~10 μm in diameter) can be seen quite readily. The micropipette technique is introduced as a progression beyond simple visualization of the emulsion drops. Observation of the remarkable stability of water-in-diluted bitumen emulsion drops, a phenomenon that greatly concerns the oil sands industry, accompanied by the use of micropipettes, is aimed to give better insights to the overall emulsion stability problem. The above combination is used to study the rigidity of water-in-diluted bitumen emulsions in this chapter. The stability concept is approached here through observations regarding interfacial rigidity.

2.2 Materials and Methods

2.2.1 Emulsion preparation

Water-in-diluted bitumen emulsions are prepared by introducing 100 μl of filtered and de-ionized water into 10 ml of diluted bitumen (1 vol.% water). This is representative of the observed concentration of water in diluted bitumen during the froth treatment process (Czarnecki, 2001). Coker feed bitumen supplied by Syncrude Canada Ltd. was used in this study. Bitumen was diluted in a solvent of n-heptane and toluene (both HPLC grade with no further purification). The mixture of toluene and heptane is referred to as "heptol". The composition of heptol is given here as the volume percent of toluene indicated in brackets. For example, heptol containing 70 vol.% toluene and 30 vol.% heptane will be denoted as "heptol[70]". To date, heptol[50], which is a 1:1 mixture by volume of n-heptane and toluene, is chosen in most cases to simulate the aromatic-aliphatic ratio of the diluent used in commercial oil sands processing (Shaw et al., 1996). Dilution of bitumen is necessary in these experiments to mirror the actual commercial process. Bitumen content in the oil phase (hydrocarbons) is expressed as a volume percentage and will be denoted by C_o. The emulsion was prepared by sonicating the mixture with a 600-watt ultrasonic probe (Sonic & Materials) for several seconds. The average drop size varied from 5 to 30 μm depending on bitumen concentration and duration of sonication. Equilibrium interfacial tension of the droplets was accomplished within few minutes after emulsification and further changes in the IFT values were not observed even after several days (Yeung et al., 1999). In this study, all emulsions were aged for 30 minutes.

2.2.2 Experimental setup

All experiments were conducted using a micropipette. Individual micrometer-size emulsion drops were manipulated using a small suction pipette. All experiments were conducted at a micron level. Thus, accuracy and repeatability were important when conducting this kind of experiments. To accomplish good accuracy, it was always ensured that the micropipette tip possessed a simple cylindrical geometry with no jagged imperfections. Initially, the micropipettes are glass capillary tubes with an outside diameter of 1mm and an inside diameter of 0.7mm (borosilicate glass; Kimble Glass Inc.). A hot wire pipette puller (David Kopf Instruments, Tujuvoa, CA) was used to draw out the capillaries under high temperature (Figure 2.1). After this treatment, one end of the capillary resulted in sub-micron tapered hollow tubes. In order to truncate squarely the tapered ends at chosen locations, a home-made forging device, shown in Figure 2.2, was used. This resulted in pipette tips having an inside diameter of 5 to 10 microns and was accomplished by fusing the pipette tip into a longer piece of glass. This is demonstrated in Figure 2.3. The long piece of glass was under high temperature, and thus in a melted form, during sinking the micropipette tip into it. Severing the pipette from the assembly after cooling completes the breaking process. The tip of the micropipette had to be treated with chemicals before use to avoid wetting by the emulsion drops. For example, to manipulate water droplets in oil, the hydrophilic nature of glass was altered into a hydrophobic one. This was accomplished by treating the glass surface with a methylating agent (e.g. dichlorodimethylsilane, applied at 20x dilution in toluene).

A schematic of micropipette setup is shown in Figure 2.4 where the real experimental setup can be viewed in the subsequent Figure 2.5. About 60 µl of an emulsion was placed in a sample cell. Microscope cover slips were used to prepare the cell, in which two sides were left open. The emulsion solution was then introduced in the cell and held there by capillary forces. A small suction pipette, mounted on a micromanipulator (Narishige, Tokyo) was then inserted into

the cell from an open side. An inverted microscope (Figure 2.6) that utilizes transmission bright-field illumination (Carl Zeiss Canada; Axiovert 100) was used for observation of the emulsion. In this manner, individual droplets could be manipulated. As it is demonstrated in Figure 2.7, grasping a droplet on the micropipette tip was accomplished by applying adjustable suction pressure at the pipette tip. This was possible by connecting the other end of the pipette (the untapered large end) to a flexible tygon tubing, the other end of which was connected to a 30 ml syringe. By using a commercial pressure transducer (Omega Engineering, Stamford, CT), the suction pressure was measured accurately. As shown in Figures 2.4 and 2.5, a video system (CCD camera, videocassette recorder and TV monitor) was connected to the microscope to monitor the micropipette experiment in real time.

2.2.3 Interfacial tension measurements

The micropipette was used to measure the interfacial tensions (IFTs) of individual emulsion drops. Individual droplets were grasped on the micropipette tip. This was possible by applying adjustable suction pressure at the pipette tip through a connected syringe. As shown in Figure 2.8, a single water droplet in an oil-continuous emulsion was held at the tip of a suction micropipette (note the curved meniscus inside the capillary). This method of IFT measurement using the micropipette technique originated from biophysical sciences (Evans and Skalak, 1980; Evans and Rawicz, 1990). From Figure 2.8, it will be demonstrated that the minimum pressure required to draw-in a droplet in an oil-filled pipette is a direct measure of the water-oil interfacial tension (Yeung et al., 1998). In the same Figure 2.8, P_1, P_2 and P_3 are the pressures developed inside the oil-filled micropipette, the water droplet and the emulsion's continuous oil phase, respectively. The critical pressure, P_{cr}, needed to drawn in the drop is given by:

$$P_{cr} = \Delta P = P_3 - P_1 \Rightarrow$$

$$P_{cr} = (P_2 - P_1) - (P_2 - P_3) \qquad (2.1)$$

Introducing here the Young-Laplace equation for spherical drops, results in the following equation:

$$P_{cr} = (P_2 - P_1) - (P_2 - P_3) \Rightarrow$$

$$P_{cr} = \frac{2\sigma}{R_p} - \frac{2\sigma}{R_o} \Rightarrow$$

$$P_{cr} = \frac{2\sigma}{R_p}\left(1 - \frac{R_p}{R_o}\right) \qquad (2.2),$$

where R_p is the pipette inner radius and R_o the radius of the droplet (Evans and Rawicz, 1990). Both R_p and R_o are easily obtained from image analysis. That is, the critical pressure P_{cr} needed to draw in a drop is related to the oil-water interfacial tension σ by the following equation:

$$\sigma = \frac{P_{cr} R_p}{2\left(1 - R_p / R_o\right)} \qquad (2.3),$$

The accuracy in obtaining the critical pressure P_{cr} is better than 1%. A droplet that has been captured will remain in a state of static equilibrium at the pipette tip as long as the suction pressure is below P_{cr}. The droplet will then rapidly enter the tube at pressures higher than P_{cr}. One can only verify the validity of the micropipette technique by measuring the interfacial tension between water and various non-polar liquids. This is also demonstrated in previous studies involving this method of IFT measurement (Moran et al., 1999; Yeung et al., 2000). The values obtained should be in agreement with those reported in the literature.

The interfacial tensions of emulsified water drops into oil solutions were measured. In this case, diluted bitumen was used instead of crude oil. The effect of bitumen concentration on the IFT values was examined by varying the bitumen concentration in the hydrocarbon phase. Also, the effect of solvent composition on the IFT values was evaluated for the different bitumen-in-solvent concentrations. That is, bitumen content in the diluent (solvent) ranges from C_o=0.001vol% up to C_o=10vol%. The role of the hydrocarbon composition on the

interfacial tension of the emulsion drops was tested by using toluene-heptane mixtures (i.e. heptol mixtures) in different ratios. More precisely, the different solvents used were: heptol[30] (i.e. heptol containing 30 vol.% toluene and 70 vol.% heptane), heptol[50] (heptol containing 50 vol.% toluene and 50 vol.% heptane) and heptol[100] (i.e. pure toluene for diluent). All measurements were taken at 22°C. Each interfacial tension value reported here is the average of three repeated experiments. In each experiment, each data point was the average IFT measurement of 8 to10 droplets.

2.2.4 Emulsion droplets deflation tests (crumpling tests)

The remarkable stability of water-in-crude oil emulsions has been attributed to the formation of a "skin" on the emulsion interface (Bartell and Neiderhauser, 1949; Reisberg and Doscher, 1956). More recent studies on water-in-diluted bitumen emulsions (Wu et al., 1998) indicate that the stabilization of emulsified water droplets is mainly due to steric repulsion between the absorbed layer on the droplet interfaces. Electrostatic forces seem to play only a minor role in comparison to steric stabilization. This steric layer can be revealed with the use of micropipettes (Yeung et al., 1999; Yeung et al., 2000; Czarnecki, 2001). For that, the following procedure was adopted: Initially, a water-filled micropipette was immersed in diluted bitumen solutions contained within the gap between the microscope slides of the micropipette apparatus. Then, a small amount of water was expelled from the pipette tip, forming a spherical droplet into the diluted bitumen. On the 10 μm scale, the formed drops were always spherical in shape. The droplet remained connected to the aqueous reservoir occupying the interior of the pipette; otherwise, the droplet will "pinch off". This can be seen in Figure 2.9a(i). In this example, the water droplet was immersed in 0.1% bitumen diluted in heptol[50]. Droplets formed in this way are allowed to age for about 3 minutes. Then, the water content of the drop was withdrawn back into the micropipette. Under these specific experimental conditions (i.e. 0.1% bitumen diluted in

heptol[50]), as the droplet was deflated and its area was decreased, the surface crumpled abruptly (Figure 2.9a(ii)). The final observed structure of the interface was very much dependent on the experimental conditions; e.g. at 10%vol bitumen in heptol[50], no crumpling of the interface was observed. It must be noted that in the absence of bitumen [thus in the absence of surfactants (i.e. in pure heptol)], no crumpling was observed. In addition, the water droplet remained spherical throughout the deflation process. Also, no crumpling of the interface was observed for 0.001%vol bitumen in heptol[50], as it is apparent in Figure 2.9b(ii).

As mentioned above, the stability of water-in-diluted bitumen emulsions is mainly due to steric effects. Furthermore, this stability and thus, this steric barrier, can be visualized with the help of the micropipette technique. Here, the behaviour of emulsion drops was observed under various experimental conditions. The role of bitumen concentration, solvent ratio and water pH in displacing surface rigidity were investigated. By varying the above experimental parameters, the crumpling and non-crumpling regimes were outlined. According to that, crumpling observations took place under the following conditions:

- Varying bitumen concentration in the diluent from 0.001% up to 10% bitumen.
- Changing the solvent ratio (i.e. toluene-heptane ratio); heptol[30], heptol[50], and heptol[100] (i.e. pure toluene) are used for different solvents.
- Changing the water pH, in the case of heptol[50] being the solvent. The water used in all experiments was filtered and de-ionized. The pH of the aqueous phase was controlled with drop-wise addition of HCl or NaOH (both from Fisher Scientific) and measured using a digital pH probe (Orion Research, Model 701A). The required amounts of acid-base in achieving the desired pH had very little effect on the ionic strength of the final aqueous phase.

2.3 Results and Discussion

2.3.1 Surfactant adsorption isotherms

The interfacial tensions of water in contact with diluted bitumen solutions were measured. IFT measurements were made to reflect variations in both bitumen concentration and solvent composition.

The micropipette technique was used to directly assess interfacial tension of individual emulsion drops. Since IFT of an emulsion drop surface is an important parameter, the pipette suction technique (see details is section 2.2.3) became the method of choice. Surfactants adsorption on the water droplet surface was characterized by mapping the IFT isotherm i.e. by plotting the interfacial tension against the bulk surfactant concentration.

Figure 2.10 shows the change in equilibrium interfacial tension σ when varying the bitumen content C_o over four orders of magnitude. Assuming diluted bitumen to be an ideal single component solution, the molar[1] surface coverage of an interface with surfactants is related to the change in interfacial tension, σ, with surfactant concentration, C_o, as follows:

$$\Gamma = -\frac{1}{kT} \cdot \frac{d\sigma}{d\ln C_o} \qquad (2.4)$$

Where Γ is the molecular surface coverage (number of absorbed molecules per unit area) and kT the thermal energy. As mentioned, interfacial tension was measured at a range of bitumen concentrations in toluene-heptane mixtures of three different toluene-heptane volume ratios.

[1] The surface coverage observed at low bitumen concentrations appears to be a monolayer coverage (Yarranton et al., 2000)

Effect of bitumen concentration

Tables 2.1 and 2.2 show a comparison between the results by the suction pipette technique and the corresponding literature values. The errors in the micropipette results are standard deviations based on measurements of 25-30 droplets. With special reference to Table 2.1, it can be seen that at very low bitumen concentrations in the bulk phase ($C_o \cong 0.001\%$), the measured IFT values varied little compared to the literature reported IFT values for the corresponding pure liquids (i.e. when no bitumen was present). This means that there was only little or no adsorbed material on the droplet surfaces. This was probably due to the very low bitumen concentration in the bulk phase, and thus, surfactant concentration on the interface. In an earlier work using the micropipette technique (Yeung et al., 1999; 2000), interfacial tension measurements had also been conducted with heptol[50] used for solvent. A comparison between results is given in Table 2.2. The obtained values from this present work seem to be lower when compared to those reported by Yeung et al. (1999; 2000). In spite of this observation, the general trend remains the same. As the bitumen concentration in the bulk phase increased, the interfacial tension of the surface of the water droplets decreased. Figure 2.10 shows that at a slightly higher bitumen concentration ($C_o \geq 0.01\%$), there was an almost linear decrease (on a semi-log scale) in IFT values when increasing bitumen concentration. This infers that the droplet surfaces were saturated by surfactants. As the bitumen content in the bulk phase increased, the surfactant concentration also increased. Thus more surfactants can now adsorb on the water-diluted bitumen interface and increasingly lower the interfacial tension on the emulsified water droplet surfaces.

Effect of solvent composition

IFT values obtained directly from the emulsion droplets surface are summarized in Figure 2.10. De-ionized water (pH~5.4-5.6) was used as the aqueous phase in these experiments. The effect of solvent composition on the interfacial adsorption of surfactants is shown in the same figure. The three solvents used are: heptol[30], heptol[50] and heptol[100] (i.e. pure toluene). For each solvent, using equation

(2.4), one can estimate the molecular cross section (i.e. area per 'site') given by the reciprocal of Γ. In an earlier work using the micropipette, molecular cross section was estimated at 0.74 nm^2 (Yeung et al., 1999). Other literature values estimate molecular cross section at saturation to be much higher, 3-5 nm^2 (Taylor, 1992; Bhardwaj and Hartland, 1994; Yarranton et al., 2000). These discrepancies are probably due to factors such as the type of crude, solvent properties and water chemistry (Yeung et al., 2000). In this study, the exact numbers of the area occupied by the surfactant molecule is not of great importance. However, it is rather interesting to note that the surface coverage, which is given by the slope of each individual line, is mainly independent of the toluene:heptane ratio of the solvent. This means that the molecular surface coverage Γ (number of adsorbed molecules per unit area) is constant regardless the solvent used. This observation is in agreement with other studies (Yarranton et al., 2000).

2.3.2 Revelation of surface rigidity through area contraction

In-situ emulsion stability was initially studied by Yeung et al. (2000) using the micropipette technique. In this latter study, stability refers to the ability of micron-sized droplets to resist mutual coalescence and coagulation. In some cases, resistance to coalescence and coagulation was even visualized through the formation of rigid interfaces that crumpled abruptly.

In the present work, surface rigidity of water drops emulsified in diluted bitumen was investigated through area contraction using the micropipette technique (for further details in section 2.2.4). Figure 2.11 summarizes the results from the contraction experiments. As in the case of IFT measurements, experiments were conducted at a wide range of bitumen concentrations in toluene:heptane volume ratios. The solvents used in this experiment were heptol[100] (or pure toluene),

heptol[70], heptol[50] and heptol[30]. Observations of Figure 2.11 lead to the following conclusions:

Effect of bitumen concentration

The rigidity of water-in-diluted bitumen emulsions was tested and the results are summarized in Figure 2.11. De-ionized water (pH=5.4-5.6) was used in these experiments. For any solvent ratio, it can be seen that at very low bitumen concentrations (C_o<0.01%) no crumpling of the interface was observed as the water droplets were deflated. Instead, they remained spherical throughout the process. As soon as bitumen concentration in the bulk increased slightly (around 0.01 vol.%) the interface of the water droplets started to crumple. Furthermore, for even higher bitumen content in the bulk phase the water droplets continued to crumple abruptly, revealing a rigid structure, which likely acted as a steric barrier (Wu et al., 1998). From these observations, it can be concluded that, when increasing surface active material in the bulk phase by increasing bitumen concentration, the surface of the water drops exhibits remarkable rigidity. Thus, when a droplet is deflated and its area is compressed, the surface crumples abruptly. Surprisingly, the crumpling phenomenon seems to disappear when increasing the bitumen concentrations, for the whole range of different solvents. It seems that for each solvent there is a distinct high bitumen concentration around which there is a shift from a crumpling to a non-crumpling regime. Similar experiments have been conducted in the past when only heptol[50] was used as solvent (Yeung et al., 1999). It was observed that crumpling disappeared when bitumen concentration was about 1 vol.%. The same trend for heptol[50] is verified in this study. Here, a wide series of experiments is conducted and the crumpling and non-crumpling regimes are more accurately mapped. It can be seen from Figure 2.11 that this critical bitumen concentration is 3vol.% when using heptol[50] as a solvent. In general, for each solvent individually, a relatively high bitumen concentration exists, around which one passes from a crumpling to a non-crumpling regime with a further increase in bitumen content.

Effect of solvent composition

The effect of solvent composition on the interfacial rigidity can be seen in the same Figure 2.11. In "good" bitumen solvents (heptol[100] or pure toluene) the crumpling phenomenon disappeared at lower bitumen concentrations than in "poor" solvents (e.g. heptol[50]). This means that emulsion rigidity was reduced in better solvents when increasing bitumen concentration. Better solvents seemed less able to maintain rigidity of the interface at relatively high bitumen concentrations.

Effect of water pH

The effect of varying the pH of the water droplets on interfacial rigidity is shown in Figure 2.12. It has been demonstrated in the past that adjusting pH significantly affects the film forming and emulsion stabilizing properties (Reisberg and Doscher, 1956; Strassner, 1968). Experiments were conducted using heptol[50] as a solvent for a wide range of bitumen concentrations and water pH (3-12). Again, what is stated in the literature can be verified with this experiment: the rigid interfacial films (crumpling regime) were formed in acidic pH. Moving along to higher pH values, these films were finally converted to mobile films in basic pH. In this particular case, it can be seen that at pH=3 the surface of the water droplets crumpled abruptly throughout the wide range of bitumen concentrations (from 0.01 to 10 vol.%). As the pH increased crumpling started to disappear at lower bitumen concentration. For example, at neutral pH the transition from a crumpling to a non-crumpling regime took place around C_o=1%. At even higher pH, the transition occurred at lower bitumen concentrations. Finally, it seems that the crumpling phenomenon (interfacial rigidity) completely disappeared at very basic pH (pH=12) for the entire range of bitumen concentrations.

2.4 Conclusions

The micropipette is introduced as a means to directly study the interfacial properties of micron-sized emulsion drops. Interfacial tension measurements and film rigidity were performed using the micropipette technique.

Natural surfactants in bitumen have the tendency to adsorb on the water/diluted bitumen interface. These are low molecular weight species which, in excess, appear to completely cover the water droplet surface and significantly lower its interfacial tension.

Interfacial tension measurement results showed that as bitumen concentration in the bulk phase (C_o) increased, the interfacial tension on the water droplet surfaces decreased. In addition, there was a little effect on the interfacial tension when using different solvent mixtures. Mixtures of toluene and heptane in different ratios were used as solvents for bitumen dilution.

Furthermore, crumpling of the interface was influenced by bitumen concentration and type of solvent. No crumpling was found for bitumen content less than 0.01% for all solvents used. This was probably due to the very low bitumen concentration in the bulk phase, and thus, surfactant concentration on the interface. Using de-ionized water (pH=5.4-5.6), crumpling was observed to occur at higher bitumen concentration. For heptol[100] crumpling disappeared at C_o>1% and at C_o>10% for heptol[30].

Finally, crumpling was strongly affected by the water pH. For the case of heptol[50], at higher pH, the crumpling region that normally occurred at C_o>0.01% disappeared. In general, pH has a very high effect on crumpling.

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Table 2.1: Interfacial tensions between water and several oil phases at room temperature.

oil phase	Literature (mN/m)	micropipette (mN/m) (Yeung et al., 1999; 2000)	micropipette (mN/m) present study
pure heptol[100]	36.1	36.0 ± 0.8	36.7 ± 0.48
pure heptol[50]	39.6	40.3 ± 0.6	40.5 ± 0.6
0.001% bitumen diluted in heptol[100]	-	-	37 ± 0.87
0.001% bitumen diluted in heptol[50]	-	41.2 ± 2.4	39 ± 0.7

Table 2.2: Interfacial tensions between water and bitumen diluted in heptol[50] at various bitumen concentrations at room temperature: Comparison with previous studies (Yeung et al., 1999; 2000) using the micropipette technique.

Co (%vol bitumen)	micropipette (mN/m) (Yeung et al., 1999; 2000)	micropipette (mN/m) present study
0.001	41.2 ± 2.4	39 ± 0.7
0.01	42.8 ± 1.2	30.4 ± 1.3
0.1	39.7 ± 0.54	26 ± 1.44
1	26.7 ± 1.43	22.1 ± 1.33
10	15.2 ± 1.15	19.1 ± 0.88

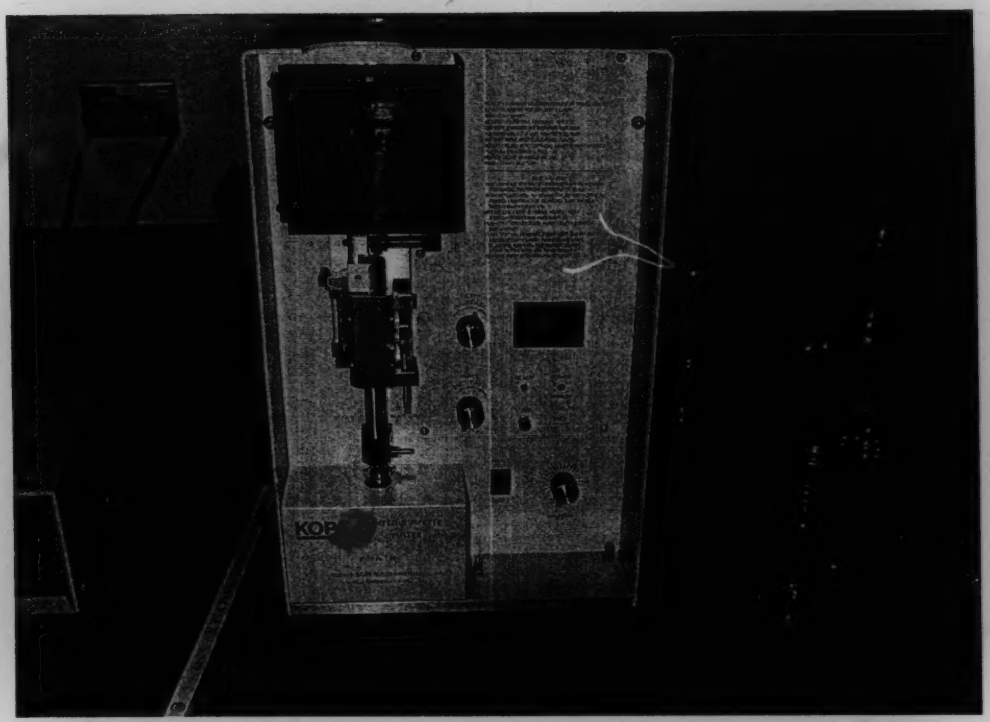

Figure 2.1: Hot wire pipette puller (David Kopf Instruments, Yujuvoa, CA) used to draw out the glass capillaries under high temperature.

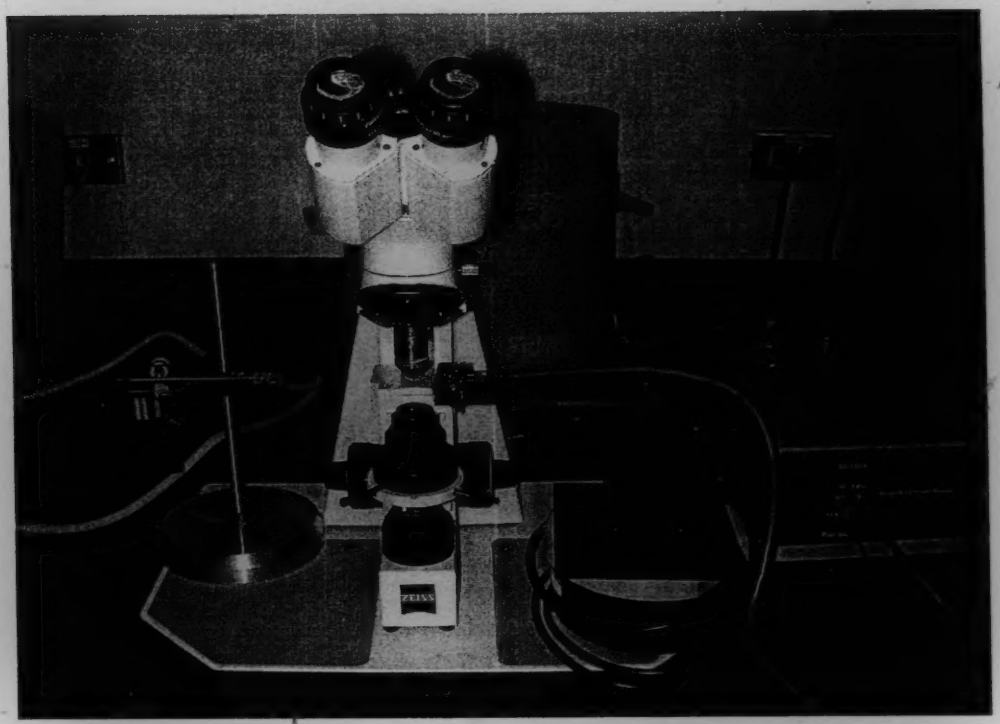

Figure 2.2: Home-made forging device for squarely truncate the tapered ends of sub-micron hollow capillary tubes.

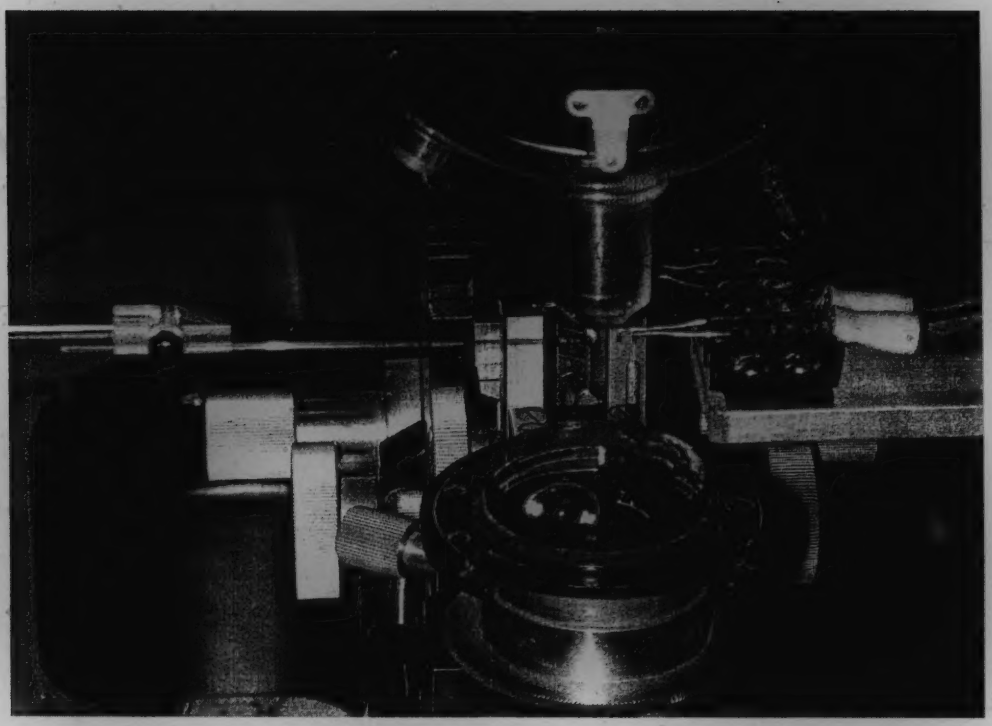

Figure 2.3: Fusing the pipette tip into a longer piece of glass. Initially, the glass pipette (left) is slowly moved towards the long piece of glass (right). The later was under high temperature, and thus in a melted form, during sinking the micropipette tip into it. Severing the pipette from the assembly after cooling completes the breaking process. The resulted pipette tip has an inside diameter of 5 to 10 microns.

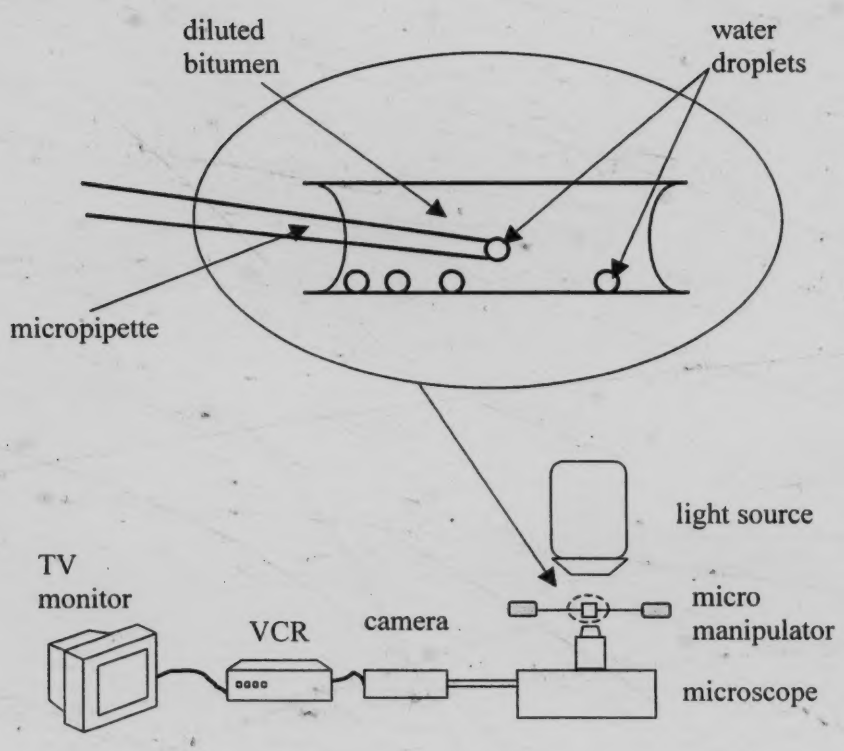

Figure 2.4: A schematic of the micropipette setup for water-in-diluted bitumen emulsions. Emulsion sample is placed in a small holding cell (also shown in the blow-up view). Water droplets can be individually manipulated by the suction pipette. Using an inverted microscope, micropipette experiments are monitored in real time and recorded on video for further analysis.

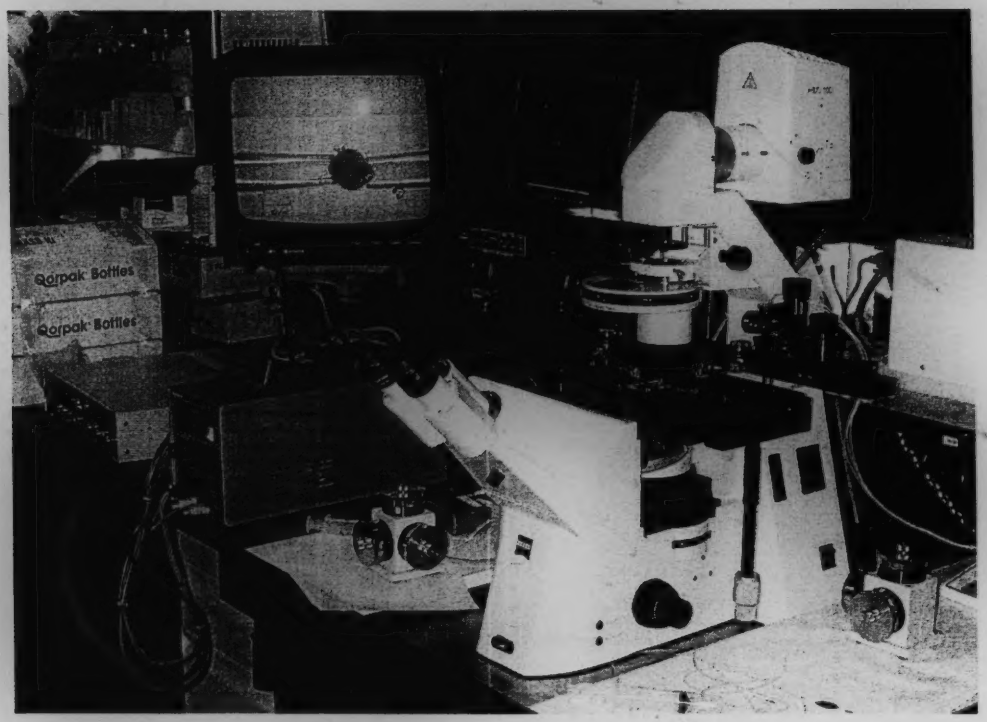

Figure 2.5: Experimental setup used to study the emulsion systems. Using an inverted microscope, micropipette experiments are monitored in real time and recorded on video for further analysis. Emulsion sample is placed in a small holding cell and is examined under bright-field illumination.

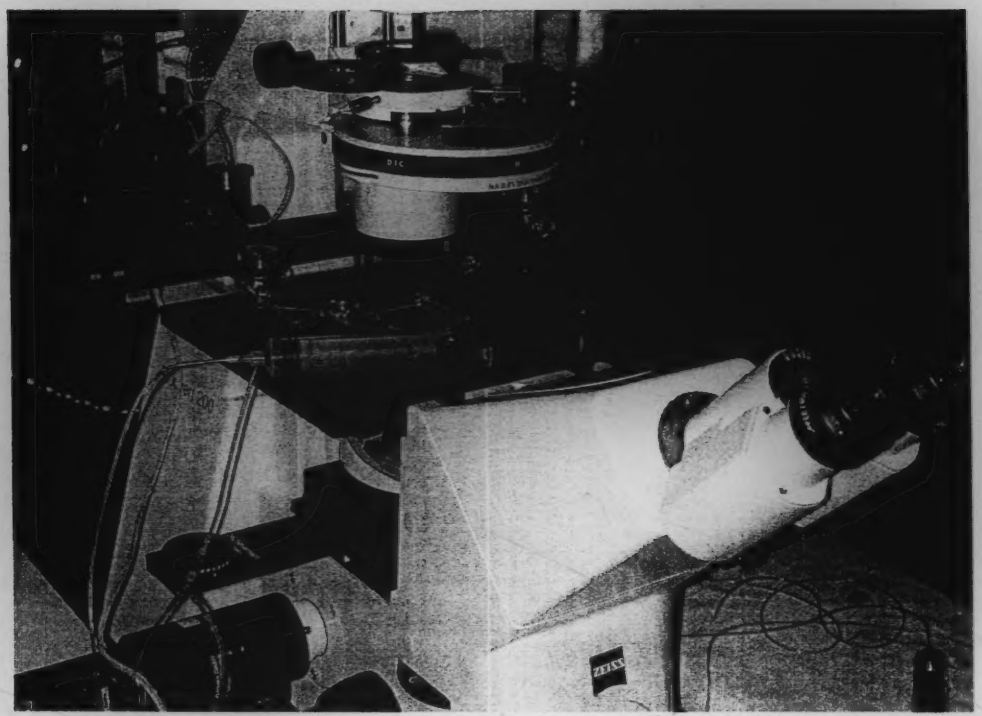

Figure 2.6: An inverted microscope that utilizes transmission bright-field illumination (Carl Zeiss Canada; Axiovert 100) was used for emulsions observation.

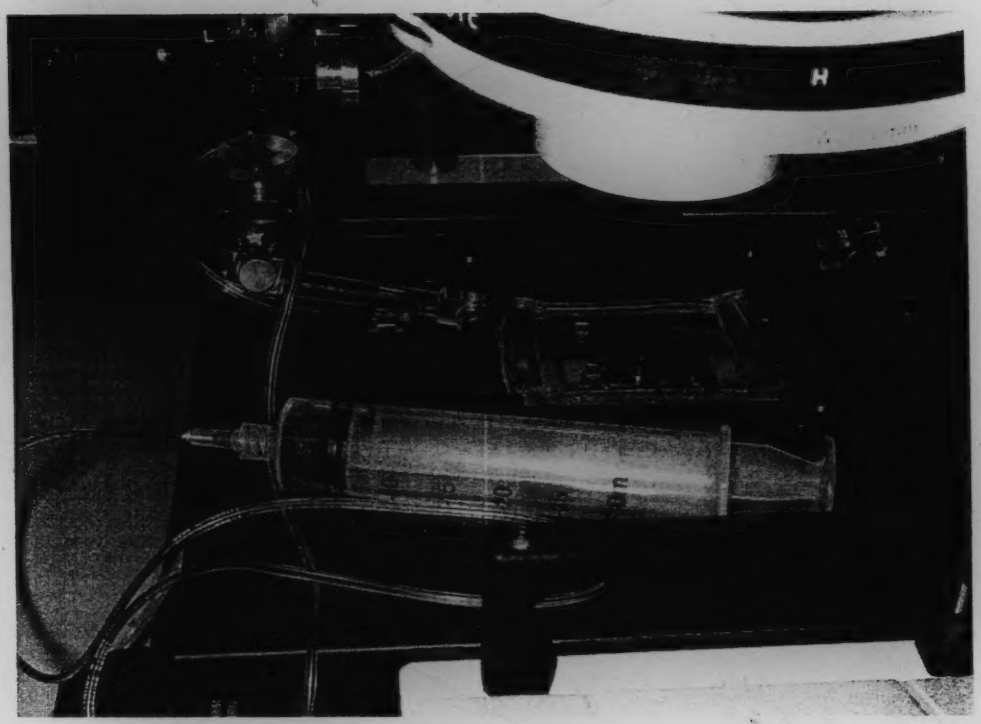

Figure 2.7: Droplets grasped on the micropipette tip by applying adjustable pressure at the pipette tip. This was possible by connecting the untapered large end of the pipette to a flexible tygon tubing. The other end of the tubing was connected to a 30 ml syringe.

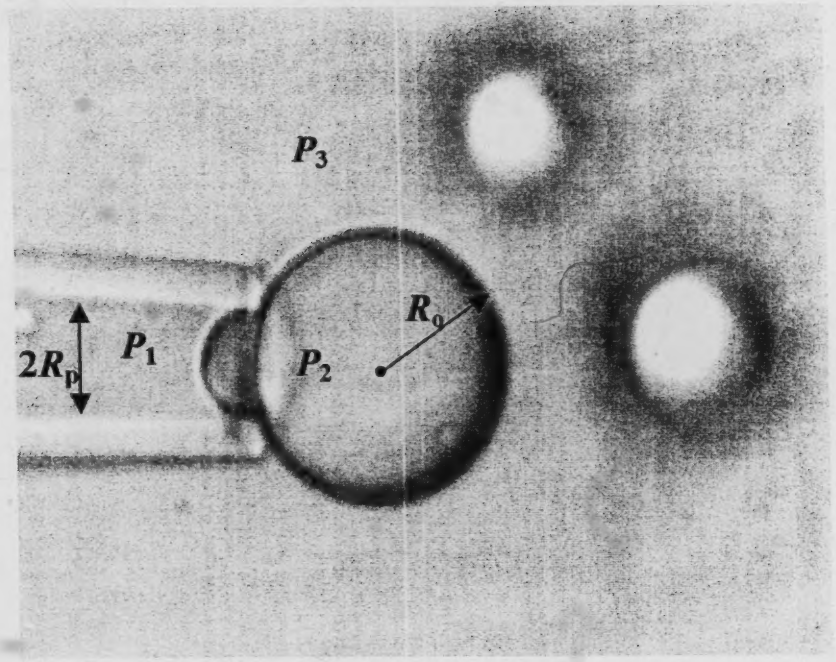

Figure 2.8: A water droplet prior to be drawn into the micropipette. Here, the continuous phase is heptol[50] (a mixture of 50:50 by volume of n-heptane and toluene). The minimum pressure required to draw-in the droplet is a direct measure of the oil-water interfacial tension (Yeung et al., 2000).

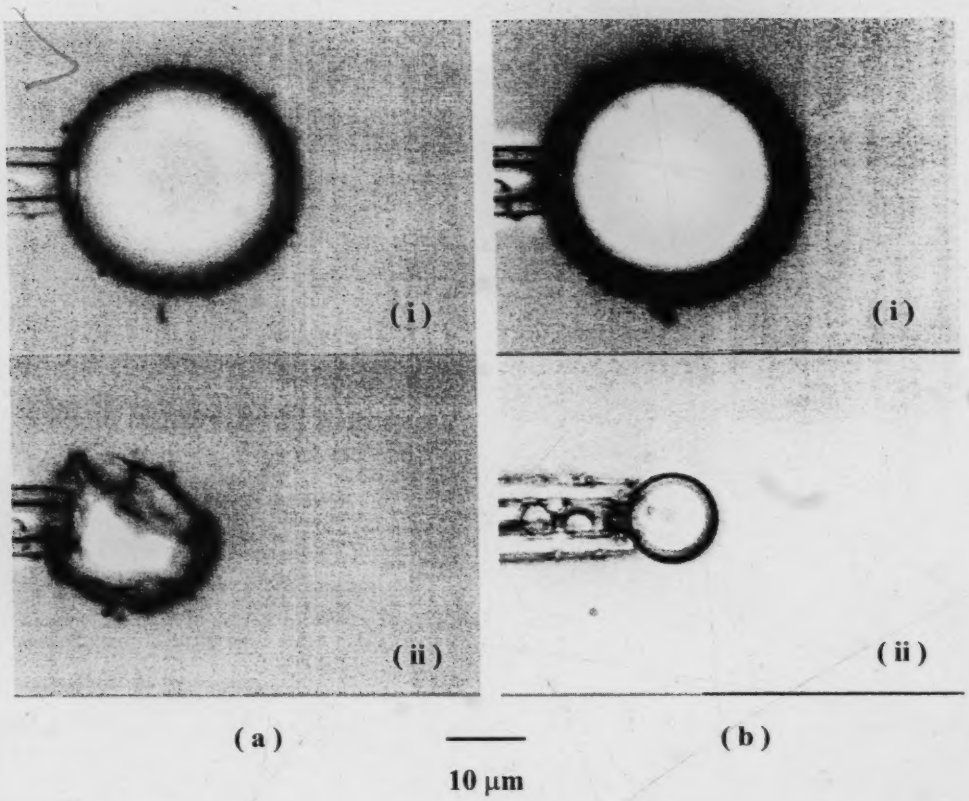

Figure 2.9: Deflating an emulsion drop using micropipette. (a) The surrounding oil phase contains 0.1% diluted bitumen in heptol[50]. The "protective" layer is revealed as the droplet area is reduced. (b) The surrounding oil phase contains 0.001% diluted bitumen in heptol[50]. No crumpling is observed; instead, the water droplet remained spherical throughout the deflation process.

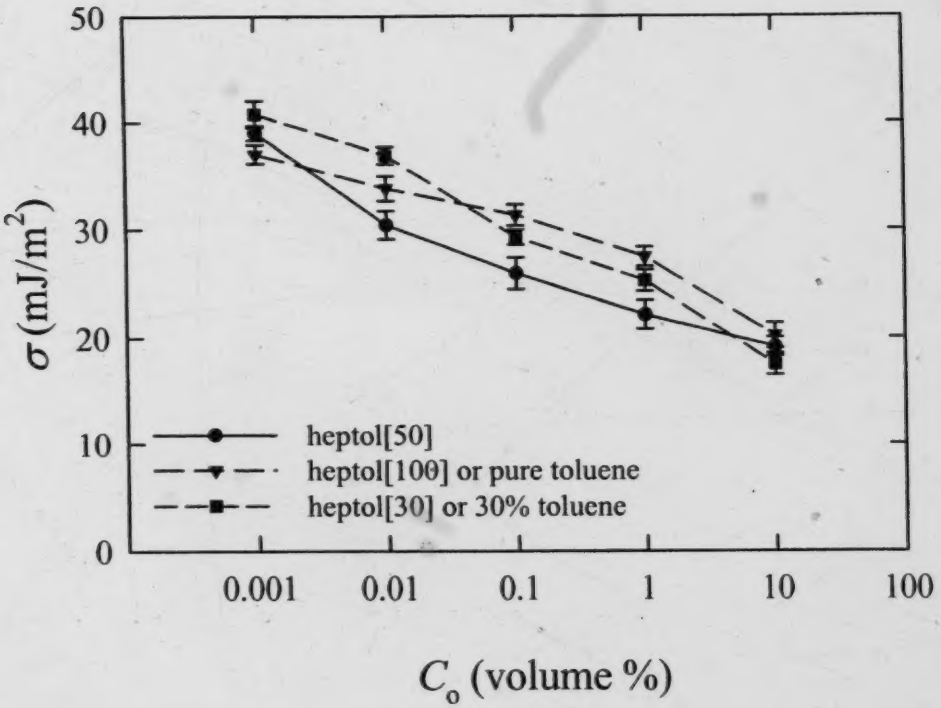

Figure 2.10: Adsorption isotherms showing the relationship between bitumen concentration and interfacial tension at different solvent ratios. The IFT values are obtained directly from the emulsion droplets surfaces (method illustrated in Figure 2.8). De-ionized water is used as the aqueous phase (pH~5.4-5.6). C_o is the bitumen content in the corresponding hydrocarbon phase. The amount of water is 1 vol% at all values of C_o. The three lines plotted refer to the three different solvents used as the continuous hydrocarbon phase.

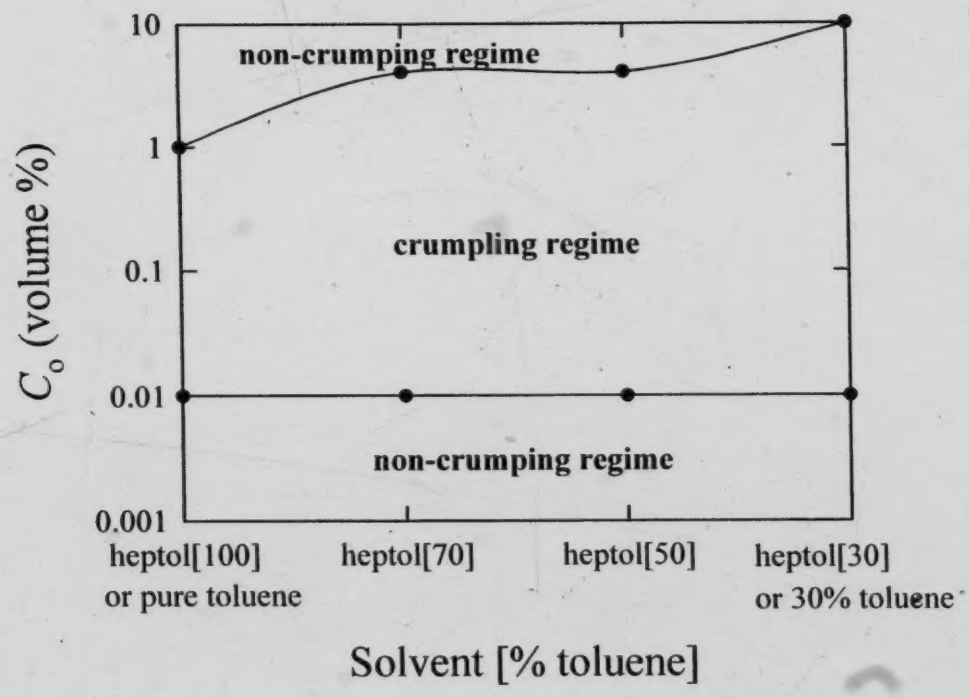

Figure 2.11: Emulsion rigidity as a function of bitumen concentration and solvent ratio. Using the micropipette technique the droplet area is reduced. The surface behaviour of the water droplets is observed when varying the bitumen concentration and the solvent used. De-ionized water is used as the aqueous phase (pH~5.4-5.6). Upon compression, the drop either remains spherical when withdrawn into the micropipette (non-crumpling regime), or reveals a rigid interface (crumpling regime).

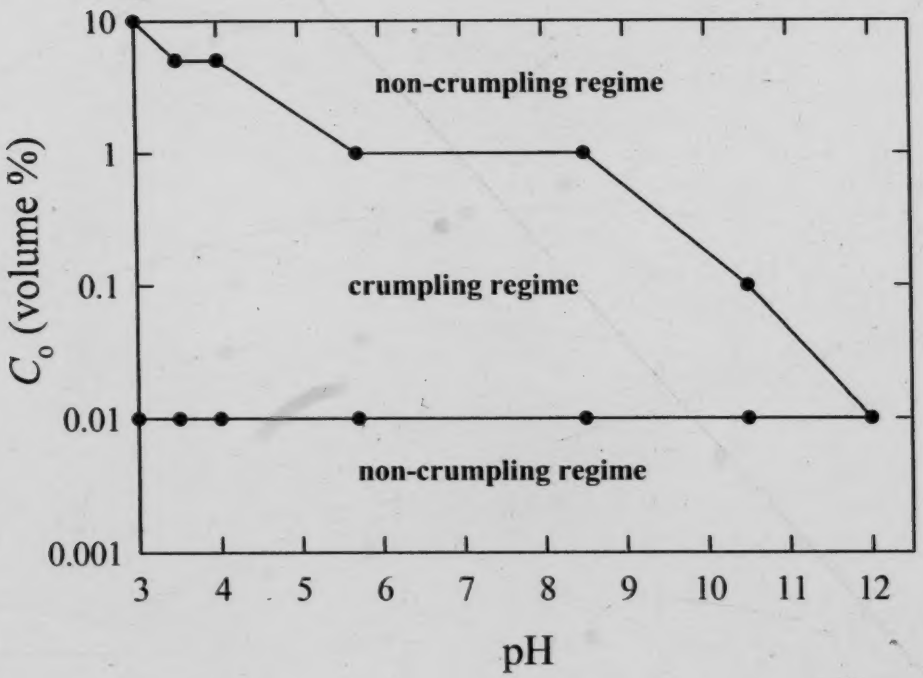

Figure 2. 12: Emulsion rigidity as a function of bitumen concentration and water pH. Using the micropipette technique the droplet area is reduced. The surface behaviour of the water droplet is observed when varying water pH and bitumen concentration. Bitumen is diluted in heptol[50]. Upon compression, the drop either remains spherical when withdrawn into the micropipette (non-crumpling regime), or reveals a rigid interface (crumpling regime).

Chapter 3

3 Bitumen-in-water emulsions

3.1 Introduction

Apart from the remarkable stability of water-in-diluted bitumen emulsions, the present interest is also concentrated on bitumen-in-water emulsions. As mentioned in the Introduction (Chapter 1), the new tailings management technique developed at Syncrude Canada Ltd. and Suncor Energy Inc. seems to cause depressed bitumen recovery under certain conditions (i.e. when processing a poor oil sands bitumen ore). It is generally believed that salts, together with an excess of clays, will cause depression in bitumen recovery during the extraction process. In order to better understand the problem, a number of investigations have been conducted in this study which are focused on the origins of the problem.

The first hot water extraction plants were patented in 1928 (Shaw et al., 1996). Clark and Pasternack (1932) first introduced the hot water separation procedure of bitumen from bitumenous sands after examining the yield of bitumen in laboratory-scale and found it to be satisfactory.

Sanford and Seyer (1979) developed a laboratory-scale batch extraction unit (BEU) at Syncrude Research in Edmonton. They used that in order to examine bitumen extraction from Athabasca oil sands and test bitumen recovery when processing the ore under various conditions (e.g., addition of NaOH, electrolytes and water temperature). It was concluded that the BEU results provided a

relatively accurate representation of what occurs on the industrial scale. This is especially true for the Clark Hot Water Extraction Process.

Takamura (1985) examined the microscopic in-situ structure of the oil sand, specifically, the way that connate water interacts with bitumen and the manner in which they are both distributed in the void space between the sand grains. He concluded that when NaOH was present in the aqueous phase, the displacement rate of bitumen from the sand is enhanced, whereas in the presence of $CaCl_2$, the sand attracts the bitumen, resulting in contact between the sand and the bitumen.

In another study, Lam et al. (1995) focused on decreasing the mean solids and water content from the bitumen froth. The hot water process and other processes operating at lower temperatures were examined along with froth samples from different depths in the froth layer. Overall, higher temperatures (~80°C) seemed to be beneficial to the bitumen recovery process.

Dai and Chung (1995) studied the bitumen-sand interaction. The effect of pH, particle size, temperature and solvent addition on bitumen-sand interaction were investigated. It was concluded that increasing the pH above 6 was always in favor of bitumen liberation. Furthermore, finer particles had a greater tendency to attach to the bitumen. Finally, it is interesting to note that, even though reduction in bitumen viscosity can be equally accomplished by high temperatures or solvent addition, the former has one more advantageous effect: apart from reducing the viscosity, it also increases the electrostatic repulsion between sand and bitumen to facilitate bitumen liberation.

A later study by Shaw et al. (1996) mostly dealt with suspensions created during the flotation process when using the Hot Water process. Shaw et al. emphasized the importance of operating the extraction process at high temperatures by pointing out that the normal hot water process temperature of 80°C is

approximately the temperature at which bitumen density difference relative to water is highest and it implies that bitumen flotation is most favorable.

To date, the extraction of bitumen from oil sands at 80°C requires large amounts of heat in the form of hot water and pressurized steam. Recently, the main target has been the development of a low energy extraction process for recovering bitumen from oil sands. The aim is to operate at about room temperature (~25°C). The work done by Mankowski et al. (1999) summarizes the different ways proposed in order to efficiently operate the extraction process at a temperature of 25°C. This will result in substantially lower energy and capital costs. The study concludes that high percentages of bitumen recovery can be achieved at lower energy consumption levels than the Warm Slurry (~50°C) and the Clark Hot Water Extraction Process (~80°C).

Kasongo et al. (2000) attempted another approach to understanding the problem of the observed reduction in bitumen recovery. The negative effect of $CaCl_2$ on bitumen recovery from oil sands had already been observed in both commercial operations and laboratory tests (Sandford and Seyer, 1979; Sanford, 1983; Smith and Schramm, 1992). To study the problem, Kasongo et al. used batch flotation tests to investigate the negative synergistic effects of calcium ions and clays on bitumen flotation recovery. Kaolinite, illite and montmorillonite were the chosen clays. He observed a sharp reduction in bitumen recovery only when calcium ions (greater than 30 ppm) were added together with 1 wt% montmorillonite clays. On the contrary, increasing calcium ion concentration up to 40 ppm, together with the addition of illite or kaolinite clays, did not interfere with bitumen flotation substantially. As a result, it became clear that the interaction of calcium with montmorillonite clays was a key parameter in the recovery of bitumen from oil sands.

Moran (2001) attempted to study the mechanics of bitumen-in-water emulsion in-situ using both the micropipette and the microcantilever techniques. These

instruments allow the manipulation of individual drops in-situ, and thus, the direct observation of the surface behaviour of the drops. In addition, measurements of important interfacial properties, like interfacial tension and interfacial viscosity, were conducted. Of particular interest was the adaptation of the micropipette technique to investigate more complex rheological behaviours. Moran (2001) examined the properties of bitumen drops in water containing calcium ions and montmorillonite clays. This particular system was chosen in order to simulate an environment detrimental to oil sands extraction. Discussion on the importance of this system was already given in the Introduction (Chapter 1). In this series of experiments, which are shape recovery experiments, Moran used the micropipettes to individually grasp bitumen droplets inside the aqueous environment of de-ionized water together with calcium ions and montmorillonite particles (DIW+M+Ca). Every single drop (only spherical drops were examined) was elongated to an arbitrary degree and after remaining in this deformed shape for 10 seconds, the drop was released. Surprisingly, the drops were not relaxing to their original spherical shape even after a long time. The drops were only partially recovering to non-spherical shapes. Since stretched bitumen drops completely recovered in the environments of either de-ionized water (DIW) or aqueous montmorillonite suspension (DIW+M), it can be inferred that only the presence of *both* calcium ions and montmorillonite clays can affect the surface plastic behaviour of bitumen drops. Moran studied the plastic behaving bitumen drops by conducting stress-strain experiments (microcantilever technique) and drop shape recovery experiments (micropipette technique). His results suggested that surface plasticity of bitumen drops is probably attributed to the adsorption of calcium-montmorillonite complexes on the surfaces of these drops. Taking one step further, he suggested that this non-ideality in the surface property was very much associated with the observed depressed bitumen recovery in the separation vessel, where the Ca^{++} in the recycled water stream from the pond is introduced. However, this single observation is not sufficient and no definite conclusions could be made at this point: the above studies dealt only with one particular montmorillonite concentration (0.1% montmorillonite in DIW) and the same

amount of calcium ions was added in all the experiments. Furthermore, Moran's experiments were conducted at room temperature (~22°C) whereas the industrial extraction process takes place at much higher temperatures (50-80°C).

The need to further investigate the combined effect of calcium ions and montmorillonite clays on the overall behaviour of bitumen drops, led to the design of a new series of experiments. This chapter of the thesis is aimed at providing further insights into Moran's novel observations.

3.2 Materials and Methods

3.2.1 Emulsion preparation

Bitumen-in-water emulsions are prepared by introducing approximately one milliliter of "coker-feed" bitumen (Syncrude Canada Ltd.) into 20 ml of aqueous solution. This mixture is then placed in a sonicator bath (Fisher Scientific, Model no. FS6) at ~50°C for two minutes and is subsequently transferred to a clean vial. Bitumen drops in the resulting emulsion ranged between 5 and 30μm in diameter. Several different environments are used as the aqueous phase:

- Filtered, de-ionized water (DIW).
- DIW, to which 50ppm of calcium ions (Ca^{++}), provided as $CaCl_2$, were added prior to emulsification. This aqueous system will be referred to as the DIW+50ppm Ca^{++} system.
- DIW, to which 0.1 wt% (based on total water) of montmorillonite clays (M) are added prior to emulsion formation. This aqueous suspension will be referred to as the DIW+M system. The montmorillonite clays were obtained from Panther Creek, Colorado, and are used as supplied from Ward's Natural Science Est.

- DIW, to which 0.1 wt% of montmorillonite clays (M) and a range of calcium ion concentrations (Ca^{++}), provided as $CaCl_2$ (Fisher Scientific), are added prior to emulsification. This aqueous suspension will be referred to as the DIW+M+Ca^{++} system. The different calcium ion concentrations used in this study were 10, 30, 50 and 100ppm. These different calcium concentrations are chosen to investigate the effects of Ca^{++} addition to the environment of DIW+M. It has been reported that the decrease in bitumen recovery, in bench-scale hot water extraction processes, occurs at 30-40ppm Ca^{++} (Kasongo et al., 2000).
- Solids-free Aurora process warm water (PW) to which 0.1 wt% of montmorillonite clays (M) are added prior to emulsification. This aqueous slurry will be referred to as the PW+M system. The Aurora process warm water was provided by Syncrude Canada Ltd., and was centrifuged at 20,000 rpm for 20 minutes for solids removal before any further use. The chemical composition of the solids-free Aurora process warm water can be seen in the Appendix A. It was noted that apart from all other chemical compounds, it also contained ~50ppm Ca^{++}. This environment was chosen for comparison purposes: it is important to investigate how bitumen droplets behave when bitumen is emulsified in both DIW+M+Ca^{++} system and in process water provided directly from the processing plant.

3.2.2 Experimental setup

The micropipette apparatus allows for the study of general mechanical behaviours of individual emulsion drops. The drop shape recovery technique was implemented. Further details about the setup may be found in section 2.2.2. In this study it was aimed to examine bitumen droplets behaviour in various emulsion environments. For that, individual micrometer-sized emulsion drops were manipulated using small suction pipettes. To study bitumen-in-water emulsions,

the pipette tip was washed in hydrochloric and nitric acids – despite the hydrophilic nature of glass – to ensure an uncontaminated surface.

A schematic of the micropipette setup is shown in Figure 3.1. As mentioned above, a more detailed description is given in section 2.2.2. All experiments were conducted within one hour of emulsion preparation at room temperature (22°C) and at a higher temperature of 50°C. When working at room temperature, no further adjustments were necessary. At a working temperature of 50°C, the microscope slide was placed under a heated stage (Figure 3.2). The temperature of the stage was fixed at 50°C by circulating hot water (Figure 3.3).

3.2.3 Drop shape recovery experiments

The purpose of this set of experiments was to study the shape recovery of deformed emulsion drops. In a drop deformation experiment, two micropipettes were used to capture the drop. This was done by applying suction pressure at the micropipette tips. Following this, with the use of micromanipulators, one of the pipettes was retracted from the other and the drop was elongated. After the drop was extended to an initial axial length L_o, it was then released from one of the micropipettes and allowed to recover to its final shape. Only drops that were initially spherical were studied here. The axial drop length L was monitored as a function of shape recovery time (t=0 defined as the moment immediately upon release of the drop). A video system (CCD camera, videocassette recorder and TV monitor) was used. The extended drop was video-recorded as it recovered, allowing for subsequent analysis. Measurements were then obtained directly from the video images. As the frame rate of the video recording equipment is $30s^{-1}$, the temporal resolution is 0.033s.

In order to conduct each experiment described above, the drop must be mechanically grasped, via suction pressure, allowing for its deformation. As a

consequence, a small projected volume of the bitumen drop is always present within the micropipette.

It has been mentioned that after the bitumen drop has been stretched to a maximum length L_o, it was then released and allowed to recover to a final shape, defined by the variable L_f that does not vary with time. Upon being stretched to a maximum length L_o, the drop was maintained in this configuration for 30s before it was released. The recovery was noted from the time at which the drop was released.

3.3 Results and Discussion

3.3.1 Behaviours of bitumen drops upon emulsification: general description

Various bitumen-in-water emulsions were prepared with the methods described above; they were then observed under an optical microscope. Initially, bitumen drops were emulsified in the following three environments:

- De-ionized water (DIW)
- DIW to which 0.1 wt% (based on total water) of montmorillonite clays (M) were added (DIW+M)
- DIW to which 50ppm calcium ions were added (DIW+50ppm Ca^{++}).

In all such environments, the emulsified bitumen drops were always spherical. This was an expected result since the drops were very small (micron-sized). It has been demonstrated in a previous study that, according to the Bond number and assuming bitumen drops to be simple and have non-zero interfacial tensions, they will be spherical as the capillary forces are significantly larger then the body

forces[2] (Moran, 2001). On the contrary, bitumen drops emulsified in the following mixtures:

- DIW containing both montmorillonite clays and calcium ions (DIW+M+Ca^{++})
- Solids-free Aurora process warm water to which 0.1 wt% montmorillonite clays (based on total water) were added (PW+M),

exhibited a very different behaviour. A significant number of drops were observed to be highly non-spherical in appearance. Still, the majority of the drops, in most cases, appeared spherical. Taking into account that bitumen is a Newtonian fluid, it is clear that some unusual mechanical phenomena occurred at the surface of the non-spherical micron-sized drops. For example, if such bitumen drops are stretched between the micropipettes and are allowed to recover, they will show minimal recovery to their initial spherical shape. Throughout this study, only bitumen drops that were initially spherical in shape were examined.

Not all the drops responded in the same manner to mechanical deformation. The behaviour of these bitumen drops was strongly dependent on the experimental conditions. Further details about the exact way that emulsion preparation influences bitumen drops behaviour will be discussed later in this chapter. In general, the following three behaviours were observed:

(a) Ideal (i.e. elastic) behaviour: upon removal of the deforming force (applied via micropipettes), bitumen drops recovered to their natural spherical shapes. This was the behaviour expected for simple emulsion drops.

(b) Plastic behaviour: the mechanically deformed drops recovered only partially from the state of maximum deformation. They did not fully recover to their initial spherical geometry.

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[2] The Bond number is given by: $B_o=\Delta\rho g R_d^2/\gamma$, where $\Delta\rho$ is the density difference between the two immiscible phases and g the gravitational acceleration. Assuming that bitumen drops are simple and have non-zero interfacial tensions (γ is ~10mN/m), for a typical bitumen-in-water emulsion of 10μm drops, B_o is $\sim 10^{-6}$, indicating that surface tension forces - which drive drops to minimum area spherical configurations - dominate over gravitational forces - that act to deform drops to non-spherical geometries

(c) Perfectly plastic behaviour: upon removal of the applied force, the initially spherical drops remained in a deformed state, with no evidence of recovery.

3.3.2 Analysis of drop shape recovery experiments

To better understand the surface rheological properties of bitumen drops and the effects of different experimental conditions on these properties, shape recovery experiments were conducted. In this study, the maximum extended length L_o and the final length L_f of the drop were observed.

Again, L_o is the maximum length that a spherical drop is extended by and L_f is final length following drop's recovery. Typically, bitumen drops recover from their stretched condition to their final shape in less than 4 seconds (Moran, 2001). This was found to be true for both perfectly elastic and plastic bitumen drops. Data were obtained for extended bitumen drops emulsified in the environment of DIW+M+30ppm Ca^{++}. Figures 3.4 and 3.5 show the recovery data for typical elastic and plastic behaving bitumen drops at 22°C and 50°C, respectively. Time t=0 refers to the time at which the stretched drop is just released from one of the pipettes and is allowed to recover. That is, at t=0, L=L_o. Referring to Figures 3.4 and 3.5, it is clear that all drops have fully recovered to their final shape within ~3s upon their release. Proceeding to the static analysis of drop shape recovery experiments, each bitumen drop was allowed to recover for at least 5 seconds before any measurement of the final length L_f was taken. This was a sufficient recovery time upon which no further recovery of the drop was observed (refer to Figures 3.4 and 3.5).

The maximum and final lengths, L_o and L_f, of bitumen drops in all the different environments (mentioned in section 3.2.1), were observed during shape recovery experiments (Figures 3.6 – 3.17). The final lengths were scaled by the drop

diameter $2R_d$. Thus, if an extended drop recovers back to a sphere, its final scaled length $L_f/2R_d$ would be close to unity. In all the plots the limiting behaviours, ideal and perfectly plastic, are plotted as solid lines. Many interesting observations can be made from the results of these experiments. First, shape recovery experiments of bitumen drops in de-ionized water (DIW) and in an aqueous montmorillonite suspension (DIW+M) will be discussed (Figure 3.6 and 3.7, respectively). Both environments indicate ideal behaviour, in that axially stretched drops always recovered back to static spherical shapes. This was also true for the environment of de-ionized water when 50ppm of calcium ions were added (DIW+50ppm Ca^{++}). It is important to note that the majority of the drops lie very close to the ideal behaviour solid line. Observations of these drops showed that they indeed recovered back to sphere. In other words, all the drops included in Figure 3.6 and 3.7 exhibited ideal response upon force withdrawal, with no signs of any unusual mechanical phenomena taking place on their surfaces. This means that deviations from the ideal response line were due to experimental errors. Error sources may be the following:

- When a drop is captured by the micropipette, there is a small fixed volume of drop fluid aspirated in the pipette. This fluid volume is not considered during the length measurements and counts for less than a few percent of the actual volume.
- The extended and the final drop lengths (L_o and L_f), as well as the diameter of the initially spherical drop ($2R_d$) are all measured with a ruler directly from the TV screen. This kind of error is estimated to be around 2%.
- Finally, the addition of montmorillonite clays may contribute to the total estimated error. A considerable amount of these clays has dimensions of up to a few microns. Montmorillonite particles may be attached on the bitumen drops surfaces throughout the experiments. That means an error in the drop length measurements, ranging from 2 to 3%.

According to the above, and taking into consideration the fact that all the drops in these two plots are observed to behave ideally, the sum of squares error (SS_E) is defined here as:

$$SS_E = \sum_{i=1}^{n}\left[\left(\frac{L_f}{2R_d}\right)_i - \left(\frac{L_f}{2R_d}\right)_{ideal}\right]^2 \quad (3.1)$$

or

$$SS_E = \sum_{i=1}^{n}\left[\left(\frac{L_f}{2R_d}\right)_i - 1\right]^2 \quad (3.2)$$

where n is the number of bitumen drops examined. The parameter SS_E can be considered a measure of the average deviation from ideal behaviour. Figure 3.7 was used for SS_E estimation. Approximately 60 drops are included in each plot.

The results of the above equations are shown in Figure 3.7 as the dashed line (parallel to the ideal behaving solid line). For better accuracy, two times the sum of square error ($2xSS_E$) was also calculated and plotted as the dotted line in the same Figure 3.7. In what follows, extended bitumen drops with final axial lengths L_f falling beyond the dotted line (two times the sum of square error line or, more simply, relative error line) are considered to behave ideally. That is, they are considered to always recover to spheres upon release of the stretching force. In contrast, bitumen drops with final axial lengths L_f above the dotted line are assumed to exhibit plastic response. In other words, they never fully recover to a natural spherical geometry. Later on in this chapter, the conditions under which extended bitumen drops behave ideally or partially plastic will be further examined and analyzed. At this stage, it seems necessary to visually understand the difference between these distinct responses. Thus, a series of photographs showing typical shape recovery experiments with bitumen drops in DIW+M+Ca^{++} systems, indicate ideal (i.e. elastic) behaviour (Figure 3.18a), partially plastic behaviour (Figure 3.18b) and permanent plasticity (Figure 3.18c). This is clear in Figure 3.18, in which the last photograph in each series represents the final, time-independent shape of the drop. It has already been mentioned that the drops are allowed to equilibrate for at least 5 seconds before their final length is measured.

As mentioned in the introduction (section 3.1), the purpose of this chapter is to discuss the effect of calcium ions and montmorillonite clays on the surface behaviour of bitumen drops. Furthermore, interesting observations regarding temperature variation during the experiments will also be reported.

Effect of calcium ion addition

The calcium ion concentrations examined were 10, 30, 50 and 100ppm. Figures 3.8–3.11 and Figures 3.12-3.15 show the bitumen drop behaviour with increasing calcium ion (Ca^{++}) concentration for T=22°C (room temperature) and T=50°C respectively. It is noted that, no matter which experimental temperature was chosen, the observed trend was the same: as Ca^{++} concentration increases, the deviation of bitumen drops from ideal behaviour also increases. With reference to room temperature (T=22°C), at the low Ca^{++} concentration of 10ppm, almost all bitumen drops behaved ideally; they recovered back to spherical shapes upon release from the tip of one of the micropipettes (Figure 3.8). That is, in Figure 3.8 the majority of the data points (every single dot represents one individually examined bitumen droplet) are below the dotted line. A quick look through Figures 3.9, 3.10 and 3.11 which correspond to 30, 50 and 100ppm Ca^{++}, leads to the observation that increase in Ca^{++} concentration enhances the plastic response of bitumen drops. Similar conclusions can be drawn when operating at 50°C (Figure 3.12-3.15).

Effect of temperature

The two temperatures under which the experiments were conducted are 22°C (room temperature) and 50°C. In this case, figures that refer to the same calcium ions concentration at two different temperatures should be compared. For example, a comparison can be made between Figures 3.8 and 3.12, both indicating the addition of 10ppm Ca^{++} at 22°C and 50°C, respectively. It may be concluded that more bitumen drops are behaving ideally at 22°C than at 50°C; that is, the majority of drops are shown as points below the dotted line at the

experimental temperature of 22°C. In contrast, a large number of data points lie above the dotted line when operating at 50°C. Continuing to higher Ca^{++} concentration, the general trend remained the same. That is, the overall behaviour is in agreement with that of 10ppm Ca^{++}: as the temperature increased, more bitumen drops surfaces appeared to exhibit a permanent distortion.

Effect of temperature on Aurora process warm water

Apart from examining the effect of temperature on the various emulsions prepared under different experimental conditions, it is also very important to investigate how bitumen drops behave in their natural environments; that is, the way bitumen drops respond to mechanical deformations (stretching every drop individually between micropipettes) when emulsified in real process water. The detailed chemical analysis of the Aurora process water used for this purpose can be seen in the Appendix A. Here, it is just noted that it consists of ~50ppm Ca^{++}. Figures 3.16 and 3.17 show the bitumen drop behaviours in the above environment at 22°C and 50°C, respectively. Both plots indicate the existence of some degree of plastic deformation of the bitumen drop surfaces. However, the overall behaviour did not entirely deviate from ideality. In addition, no further conclusion can be made at present regarding which plot (thus, which temperature) appears to be more detrimental to bitumen drops final response. Taking into account that Aurora process water consists of ~50ppm Ca^{++}, a quick glance at Figures 3.10 and 3.14, which correspond to 22°C and 50°C when de-ionized water (DIW) was used, led to the following observation: permanent deformation of bitumen drop surfaces was far more prominent in the environment of DIW than when emulsified in Aurora process warm water.

3.3.3 Effects of temperature and calcium ions addition on the number of plastically behaving bitumen drops

In the previous section, a definition has been given regarding to what one should consider as ideally or as non-ideally behaving drops; the relative error has been calculated and plotted as the dotted line, parallel to the ideally behaving line, in Figure 3.7. This dotted line, which can be seen in Figures 3.6-3.17, will be the basis for further discussion. Taking Figure 3.7 for example, regardless of the exact position of each data point (and thus, each stretched drop) on the plot, all drops below the dotted line are considered to behave ideally (i.e. always recover back to a sphere), whereas data points above the dotted line will always be considered plastically deformed drops (non-ideal behaving drops). Based on that definition and taking Figures 3.6-3.17 into account, a summary of the experimental results can be seen in Figure 3.19. The x-axis represents the calcium ion concentration in ppm of Ca^{++} added, whereas y-axis, N_p, stands for the fraction of bitumen drops lying above the dotted line with respect to the total number of stretched drops. It is clear that as Ca^{++} concentration increases, the number of bitumen drops that behave plastically also increases. The same trend was observed when temperature was increased from 22°C to 50°C. More drops appeared to exhibit permanent distortion from their original spherical shape at 50°C. However, when using Aurora process water, the opposite trend exists. A higher number of plastic drops was obtained at room temperature (T=22°C) than at the higher temperature of 50°C. In short, increases in both Ca^{++} addition and temperature seem to enhance the bitumen drops' permanent shape deformation in the environment of de-ionized water to which 0.1 wt% montmorillonite clays have been added (DIW+M+Ca^{++} systems). In contrast, a more ideal overall response was observed when the same temperature increase was implemented for Aurora process water.

3.3.4 Effects of temperature and calcium ions addition on the degree of plasticity of bitumen drops

In the previous section, bitumen drops were roughly sorted into two categories: ideally behaving and plastically behaving drops. This classification was based on the definition of a plastic drop given in that same paragraph; drops above the estimated relative error line are considered plastic. In this section, a first order approximation concerning the magnitude of shape deformation of bitumen drops will be made. For example, in Figure 3.12, both A and B data points can be considered plastic according to the above definition for plasticity. At the same time, those two drops, even though they were stretched at about the same maximum length (distance $L_o/2R_d$), their final recovery shapes seemed to be very different. Drop B has a final position closer to the line of perfectly plastic response. That is, drop B is "more plastic" than drop A with a higher value of scaled final recovery length, (scaled length, $L_f/2R_d$). Thus, drop B has a higher degree of plasticity. In order to characterize further this observed diversity in the final drop recovery length ($L_f/2R_d$), the drops should have been subjected to the exact same amount of stretching ($L_o/2R_d$). In other words, comparisons among final drops deformation ($L_f/2R_d$) should be done for equally stretched drops ($L_o/2R_d$). This may be true for the two drops A and B in Figure 3.12 but, in general, all the experiments took place by randomly stretching each drop between the two micropipettes and letting the drop recover to its final shape. No particular focus was given in subjecting the bitumen drops to the exact same amount of initial stretching. Thus, the amount of drop stretched along the $L_o/2R_d$ axis is plotted in Figure 3.20. The scaled maximum drop stretching length ($L_o/2R_d$) was arranged at equal intervals. The y-axis refers to the frequency of droplets included in each particular interval. That is, the y-axis represents the initial drop stretching frequency. Each individual line plotted in Figure 3.20 represents each one of Figures 3.6-3.17. That is, Figure 3.20 is a summary of Figures 3.6-3.17 regarding the amount of initial deformation of the drops. Concentrating on this last Figure 3.20, each plot represents an individual series of experiments. These plots overlap

each other to a large extent. Furthermore, all plots have peaks that are in the same narrow range of $L_o/2R_d$ (1.3 to 1.5). That is, regardless the experimental conditions, the majority of the drops were stretched at roughly the same maximum scaled length $L_o/2R_d$. This allows for further comparisons regarding the final recovery scaled lengths $L_f/2R_d$ of the more-or-less equally stretched bitumen drops. In addition, statistical analysis results (Appendix B) indicated that, throughout the various experiments, the stretched drops appear to fall under the same mean. That is, in all the experiments, the drops are stretched in a fairly consistent way. According to that, the $L_f/2R_d$ value of every data point throughout Figure 3.6-3.17 was taken into consideration and the results were demonstrated in Figure 3.21. The x-axis refers to calcium ions concentration in ppm of Ca^{++} and y-axis stands for the degree of plasticity defined as:

$$\text{Degree of plasticity} = \frac{\sum_{i=1}^{n}\left[\left(\frac{L_f}{2R_d}\right)_i - \left(\frac{L_f}{2R_d}\right)_{ideal}\right]}{n} \times 100 \qquad (3.3),$$

where n is the number of stretched bitumen drops included in each one of Figures 3.6-3.17[3]. The above can be simplified to give:

$$\text{Degree of plasticity} = \frac{\sum_{i=1}^{n}\left[\left(\frac{L_f}{2R_d}\right)_i - 1\right]}{n} \times 100 \qquad (3.4)$$

From Figure 3.21, it is obvious that increasing both calcium ions concentration and/or temperature also increased the degree of bitumen drop plasticity in the environment of de-ionized water to which 0.1 wt% montmorillonite clays were added (DIW+M+Ca^{++} systems). That is, the mechanical properties of bitumen drops were far from ideal (upon their mechanical deformation) in the environment of DIW+M+Ca^{++}. However, bitumen drops emulsified in Aurora process warm water to which 0.1wt % montmorillonite clays were added (PW+M system) had

[3] Approximately 60 drops are included in each Figure 3.4-3.15

roughly the same degree of shape deformation upon stretching. Temperature increase did not affect the final recovery length of bitumen drops elongated in PW+M systems.

3.3.5 Possible explanation of the overall increased surface plasticity with increasing calcium ions concentration in DIW+M+Ca^{++} systems

As seen in Figures 3.19 and 3.21, which summarize all the experimental results, both the N_p (i.e. fraction of plastic behaving drops) and the degree of plasticity of bitumen drops increased with an increase in calcium ion concentration. In general, this plastic surface behaviour of bitumen drops is revealed only in the presence of both calcium ions and montmorillonite clays. It has been suggested that the aqueous montmorillonite slurry changes upon the addition of small amounts of calcium, as the clays appear to swell or aggregate (Moran, 2001). The latter has also been observed during this study. It seems that when dealing with aqueous systems of de-ionized water to which montmorillonite clays and calcium ions have been added, the monovalent sodium ions, which are originally associated with montmorillonite, exchange with divalent calcium ions. As a consequence, a free cationic site is created and the sub-micron calcium-montmorillonite (CaM) aggregates are attached onto the negatively charged bitumen drop surfaces[4]. As the bitumen drop is elongated between the micropipettes, CaM complexes are allowed to adsorb onto the freshly created interface. After certain duration[5], the drop is allowed to recover. However, the drop surface is now occupied by new CaM complexes, which approach one another during the drop's recovery. These CaM complexes may be compressible to a certain degree and thus, the shape recovery comes to an end as these complexes saturate the interface. The drop will stop recovering even though it is still non-spherical. This possible mechanism,

[4] Numerous studies report the negative measured zeta potential of bitumen droplets

[5] The stretching time during all the experiments is 30 seconds

due to which bitumen drops surfaces exhibit plastic behaviour, has been proposed in previous a study (Moran, 2001) and is adopted here as well.

In addition, this study reveals an increase in bitumen droplets plasticity with increasing Ca^{++} concentration. A possible explanation is that, in the presence of excess calcium, more free cationic sites are present on the CaM complex. Again, as the drop surface is extended between the micropipettes, the larger CaM complexes are adsorbed on the freshly created interface. It is possible that the larger and more positively charged CaM aggregates will adsorb on the negatively charged bitumen drop surface in a more efficient way; large CaM aggregates may have many points of attachment with the bitumen surface, leading to a more flat configuration of CaM complexes on bitumen drops surfaces. The drop, which is then allowed to recover, is now saturated with well-attached large CaM complexes. As the adsorbed complexes come in contact with one another, the recovery of the drop will stop. In this case, the increased number of CaM complexes on the bitumen drop surface further inhibits the recovery of the initially spherical drops. As a result, an increased number of plastic drops accompanied by higher degree of plasticity on their surfaces is observed as the calcium ion concentration in the DIW+M+Ca^{++} systems increases.

3.3.6 Possible explanation of the overall increased surface plasticity with increasing temperature in DIW+M+Ca^{++} systems

It can be seen in Figure 3.19 and 3.21 that increasing the temperature from 22°C to 50°C results in enhancing the number of plastic bitumen drops and their degree of plasticity. A possible mechanism explaining the plasticity phenomenon on bitumen drops surfaces has already been proposed in section 3.3.5: positively charged CaM complexes may adsorb onto the negatively charged drop surface. It has been reported that at pH values of 5-6 (which corresponds to the pH value of

DIW), an increase in temperature from 22°C to 50°C results in a similar increase in the negative zeta potential of bitumen droplets (Dai and Chung, 1995). In other words, increasing the temperature in the present DIW+M+Ca^{++} systems should result in a more negatively charged bitumen surface. As a consequence, the amount of positively charged CaM complexes adsorbing on the more negatively charged bitumen surface may increase. Thus, the recovery of the bitumen drop will be inhibited by a larger amount of CaM complexes concentrated on its surface. Overall, more drops will exhibit plastic behaviour with higher degree of plasticity observed.

3.3.7 Possible explanation of surface behaviour in process water (PW+M systems)

The need to examine the effect of temperature in an environment that approaches the real industrial process led to the use of the Aurora process water to which 0.1 wt% (based on total water) montmorillonite clays had been added. The experimental results for the Aurora water can also be seen in Figure 3.19 and 3.21. It seems that, although the process water (PW) system contains ~50ppm Ca^{++} (an extended chemical analysis is given in Appendix A), its behaviour is quite different from the DIW+M+50ppmCa^{++} system, for both temperatures. The values of N_p and/or the degree of plasticity for the PW systems are closer to the DIW+M+Ca^{++} systems where 10-30ppm Ca^{++} were added. It thus appears that when PW+M is used as the continuous phase, bitumen droplets do not exhibit any remarkable plastic behaviour. Overall, the system of PW+M is observed to be less plastic than the DIW+M+Ca^{++} system containing the same amount of calcium ions. In addition, temperature does not drastically affect the plastic behaviour of these PW+M systems.

First, a possible explanation of the observed "mild" plastic behaviour of bitumen drops at 50ppm Ca^{++} will be given with reference to the chemical analysis of the Aurora process water (Appendix A). Apart from ~50ppm Ca^{++}, the process water also contains a considerable amount of sodium ions (Na^{+}). Similar monovalent sodium ions are originally associated with the montmorillonite clays, before the latter are added to the aqueous calcium solution. Upon addition of M clays to the DIW+Ca^{++} solutions, the monovalent Na^{+} ions associated with the M clays are exchanged with divalent Ca^{++} ions existing in the aqueous phase. In the case of PW, the aqueous phase consists of many different ions including considerable amounts of sodium and calcium ions. It may be that Na^{+} ions are competing with Ca^{++} ions in occupying the montmorillonite clay surface. Thus, available montmorillonite sites in PW+M system are occupied with not only Ca^{++} ions (as in DIW+M+Ca^{++} systems) but also Na^{+} ions originating from the aqueous phase. In conclusion, the smaller amount of Ca^{++} ions associated with montmorillonite probably leads to less aggregation of such clays. Thus, fewer and smaller CaM aggregates will adsorb on the freshly bitumen surface created during bitumen drop elongation. As a result, there is an observed decrease in the number of plastic bitumen drops (N_p also decreases) and degree of plasticity when PW is used in the place of DIW.

On the other hand, as mentioned earlier in this section, varying the temperature does not seem to influence the PW+M system plastic behaviour. It has been reported that at pH values around 8 (which also represents the pH of the Aurora process water), increasing the temperature from 22°C to 60°C made no difference in the zeta potential of bitumen droplets; that is, the zeta potentials of bitumen drops at pH=8 measured under two different temperatures gave the same value (Dai and Chung, 1995). It seems that at pH=8, and in contrast to pH=5-6 for DIW, increasing the temperature does not change appreciably the surface charge of bitumen drops. The formed CaM aggregates exhibit similar degrees of attachment with bitumen drops surfaces and probably adsorb on them under the same configuration at both operating temperatures. Overall, similar values for the

fraction of plastic bitumen drops N_p and degree of plasticity are obtained upon mechanical deformation of bitumen drops emulsified in PW+M systems for the two temperatures.

3.3.8 Stability observations related to calcium ions addition

It has been demonstrated than increasing the Ca^{++} concentration in DIW+M+Ca^{++} systems leads to further deviation from ideality. It is speculated that the increased number of CaM complexes adsorbing on bitumen drop surface does not allow individually stretched bitumen drops to recover back to their natural spherical shape. The observed permanent surface distortion of bitumen drops, which is most likely due to the accumulation of CaM complexes on drops surfaces, is probably very much related to the stability of such emulsion systems. Figure 3.22 shows a series of photographs (top to bottom) depicting the stability of bitumen-in-aqueous slurry emulsions at 22°C. In general, with the ability to manipulate micron-sized bitumen drops under in-situ emulsion conditions, the stability of a two-droplet system can be simply tested by capturing each droplet with a micropipette and bringing them into contact. The two series of photographs in Figure 3.22 refer to emulsified bitumen drops in (a) DIW+M and (b) DIW+M+100ppm Ca^{++} systems. A bitumen drop, which is captured at the micropipette tip, and a larger drop (visible in the background) can be distinguished at the top photograph in Figure 3.22a. The large drop is approaching the smaller drop; some movement may be due to small suction pressure at the tip of the other immersed micropipette. Following the sequence of pictures in Figure 3.22a, it can be seen that the bitumen droplets dispersed in de-ionized water to which montmorillonite clays are added (DIW+M system) do readily coalesce upon contact (bottom photograph). However, with the addition of calcium ions in the continuous aqueous phase, the resulting bitumen-in-water emulsion becomes remarkably stable. Figure 3.22b demonstrates such an observed stability when 100ppm Ca^{++} are added in the previous system (DIW+M+100ppm Ca^{++}). It is

clear that despite attempts to induce coalescence through forced contact for relatively long time, the droplets remain separate entities. The flattened contact region had a typical radius of several microns. As the two droplets were pulled apart, no sign of interdroplet adhesion was evident (bottom photograph). The resistance to coalescence, upon addition of calcium ions to the continuous emulsion phase, is in itself a serious impediment to the recovery of bitumen from oil sands. It seems that the addition of calcium ions leads to the formation of CaM complexes or aggregates which, in turn, create an adsorbed film that is capable of preventing both coalescence and coagulation of the bitumen droplets. Clearly, more work is required to provide further validation of this proposed mechanism regarding the observed resistance to coalescence and coagulation.

3.4 Conclusions

Micropipette techniques have been developed to study the rheological behaviours of emulsion drop surfaces. The experiments involved micron-scale shape recovery experiments in which an individual drop is elongated between micropipettes and, upon release from one of the pipettes, is allowed to recover to its final shape.

Aqueous solutions of de-ionized or process water (DIW or PW), both containing montmorillonite clays (M) and/or calcium ions (Ca^{++}) were used in the experiments. It is apparent that the presence of both calcium ions and montmorillonite clays played a role in the plastic behaviour of bitumen drops. The effect of temperature and calcium ion addition on the various emulsion systems was also investigated.

Regarding DIW+M+Ca^{++} systems, an increase in both temperature and calcium ion concentration resulted in a similar increase in the number and the degree of plastic bitumen drops.

On the other hand, bitumen drops in PW+M systems exhibited no significant overall plasticity of their surfaces even in the presence of considerable amounts of Ca^{++} ions and/or at higher experimental temperature. It seems that both calcium and sodium ions contained in process water compete with each other to occupy the montmorillonite clay surface. In addition, at the pH value of process water ($pH \cong 8$), increasing the temperature did not change the value of bitumen droplet zeta potential.

Lastly, the stability of bitumen-in-water emulsions at 22°C was demonstrated. It was observed that bitumen droplets coalesced upon contact in the DIW+M system. The addition of calcium ions (Ca^{++}) to such a system led to the inhibition of both coagulation and coalescence of the bitumen droplets; this may be due to the formation of CaM aggregates at the bitumen-water interface.

3.5 References

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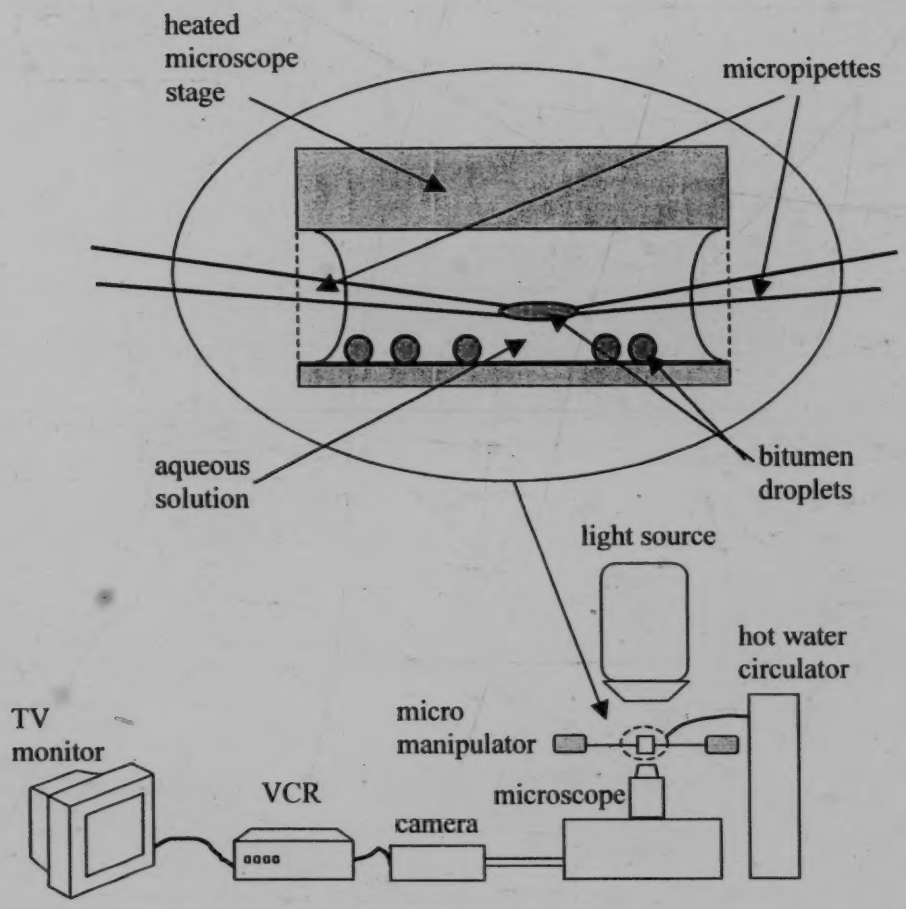

Figure 3.1: A schematic of the micropipette setup for bitumen-in-water emulsions. Emulsion sample is placed in a small holding cell (also shown in the blow-up view). The microscope cell is placed on a heated microscope stage when controlling the experimental temperature. The temperature of the stage is controlled by hot water circulation. The bitumen drops can be individually manipulated by two suction pipettes. Using an inverted microscope, shape recovery experiments are monitored in real time and recorded on video for further analysis.

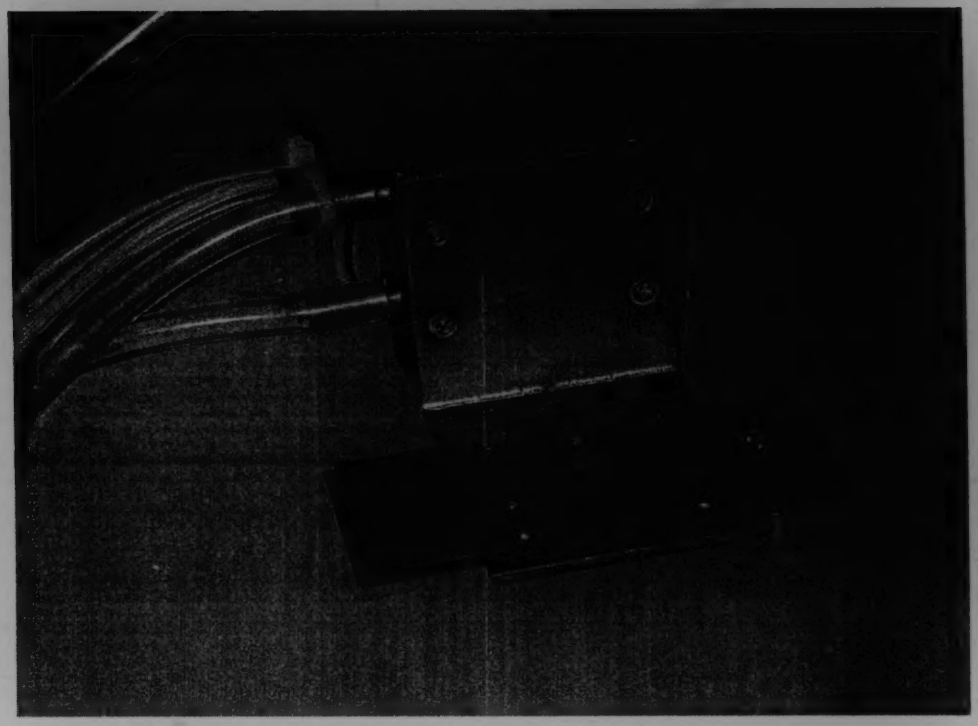

Figure 3.2: Heating stage used for conducting experiments at the higher temperature of 50°C. The emulsion sample was introduced to the microscope cell which, in turn, was placed under the heating stage.

Figure 3.3: Hot water circulator used for controlling the temperature of the heating stage.

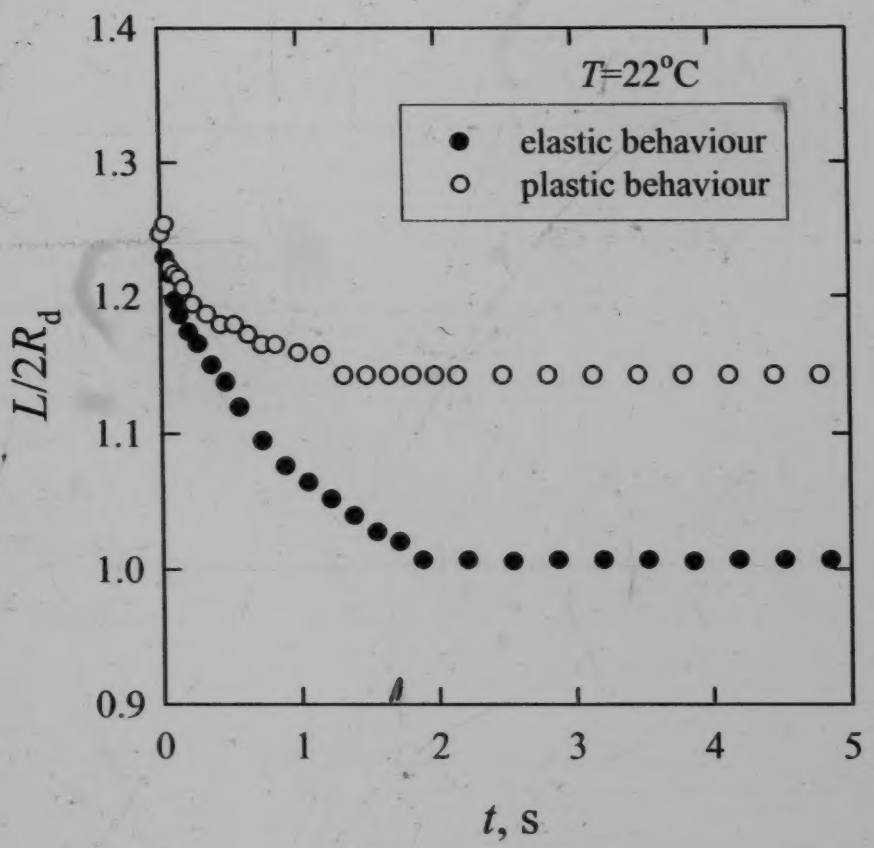

Figure 3.4: Typical dynamic drop shape recovery data for extended bitumen drops at 22°C. In this case, the aqueous phase is DIW+M+30ppm Ca^{++}. The dynamic drop length is scaled by the drop diameter $2R_d$. The experimental data describe the shape recovery of two different drops: an elastic (i.e. ideal) and a plastic behaving bitumen drop.

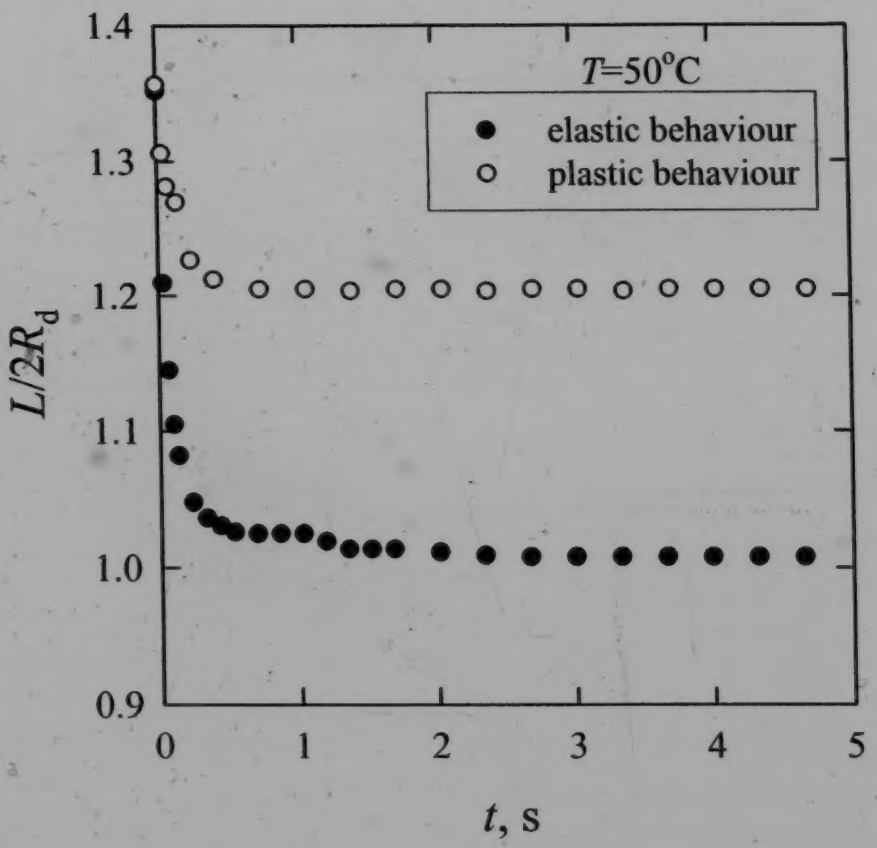

Figure 3.5: Typical dynamic drop shape recovery data for extended bitumen drops at 50°C. In this case, the aqueous phase is DIW+M+30ppm Ca^{++}. The dynamic drop length is scaled by the drop diameter $2R_d$. The experimental data describe the shape recovery of two different drops: an elastic (i.e. ideal) and a plastic behaving bitumen drop.

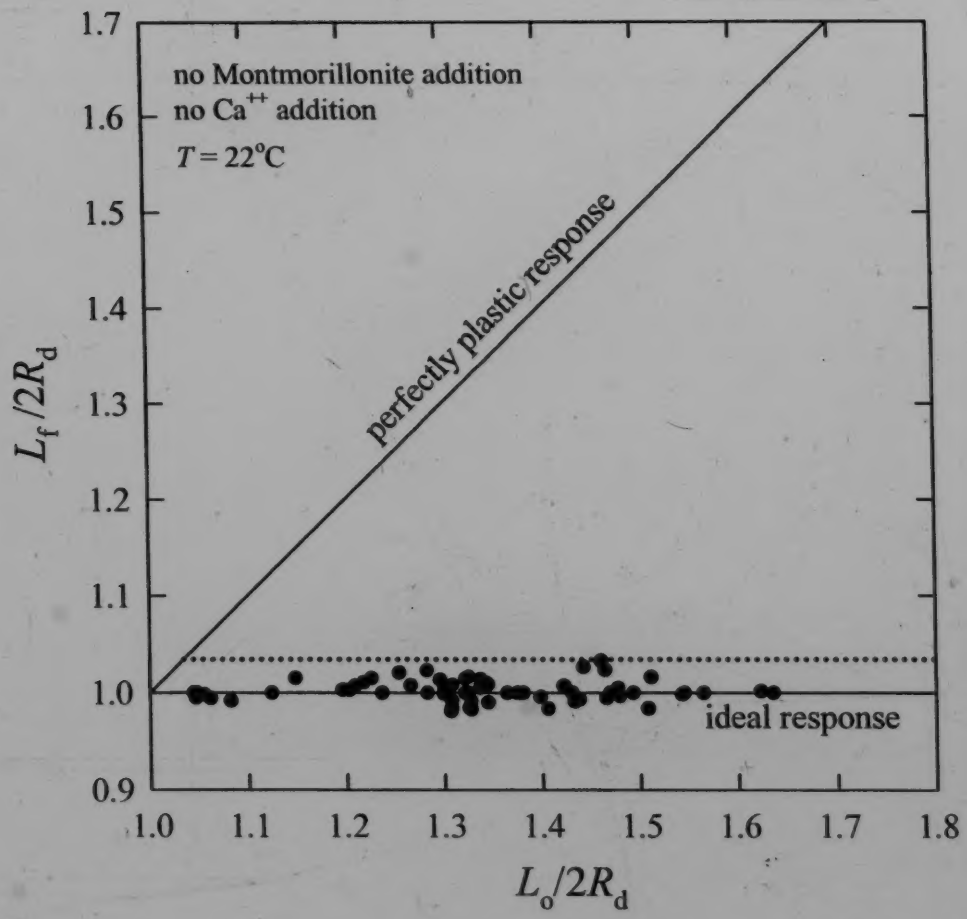

Figure 3.6: Static analysis of drop shape recovery experiments for bitumen drops in DIW at 22°C.

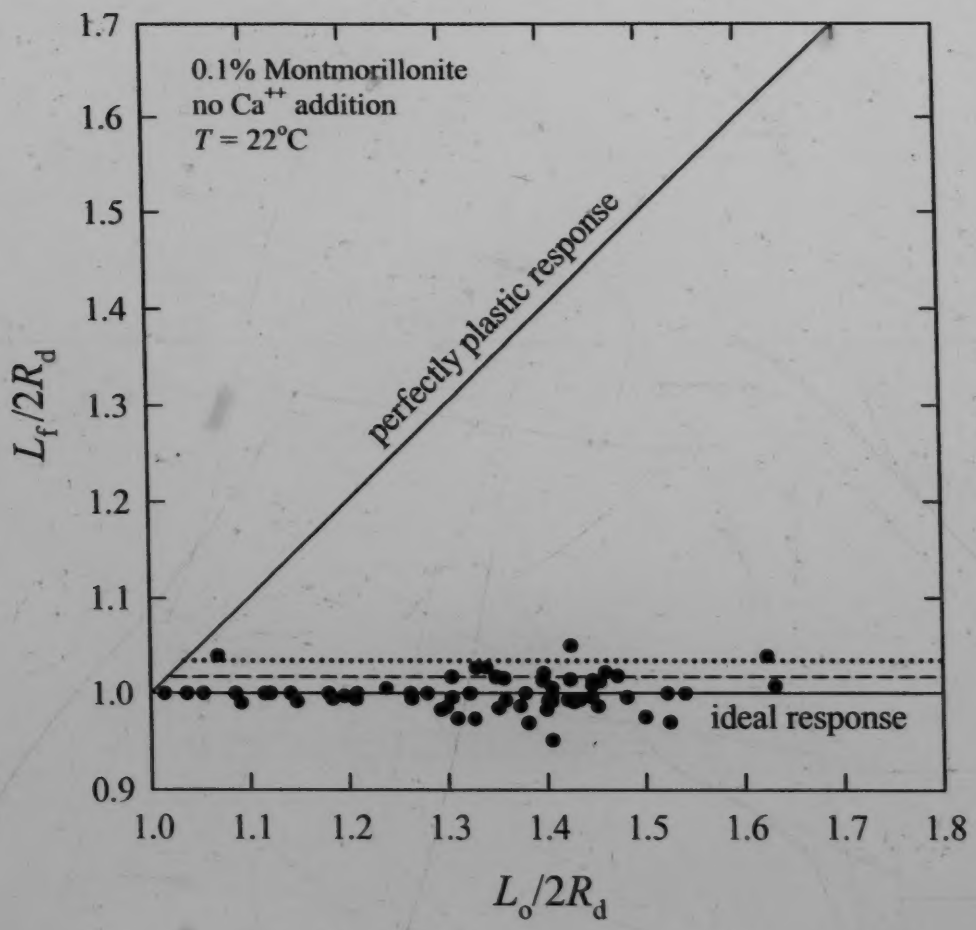

Figure 3.7: Static analysis of drop shape recovery experiments for bitumen drops in DIW+M at 22°C.

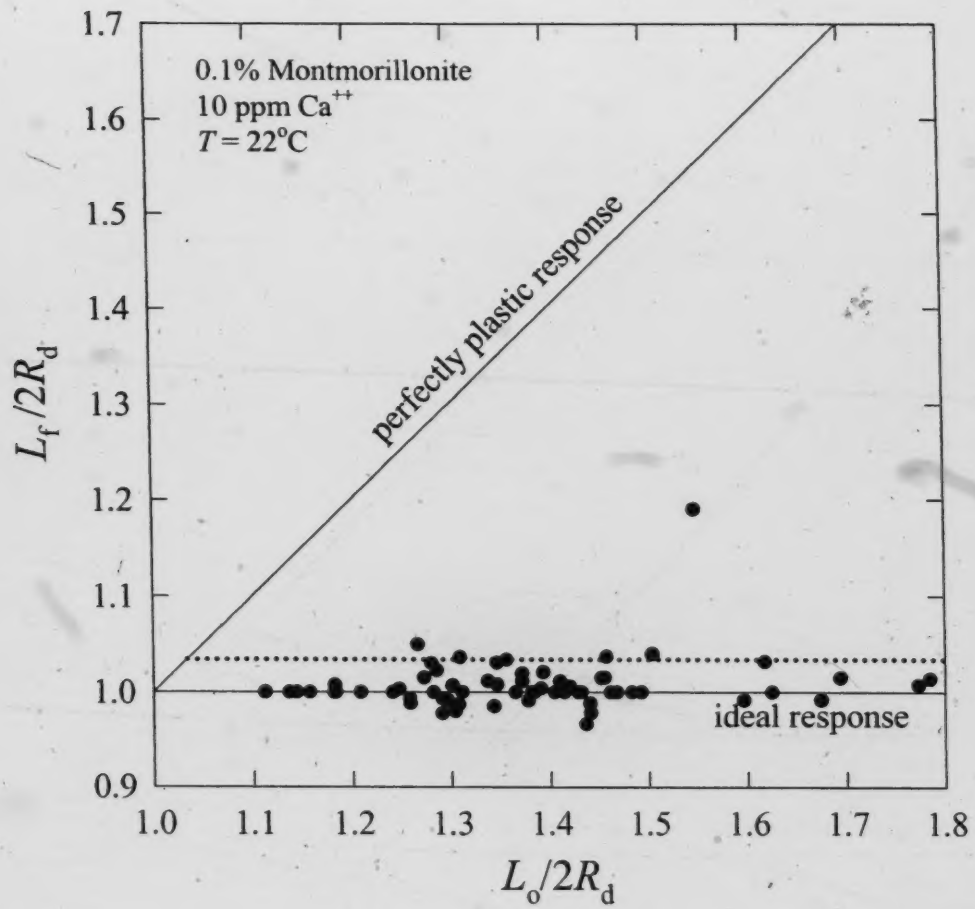

Figure 3.8: Static analysis of drop shape recovery experiments for bitumen drops in DIW+M+10ppm Ca^{++} at 22°C.

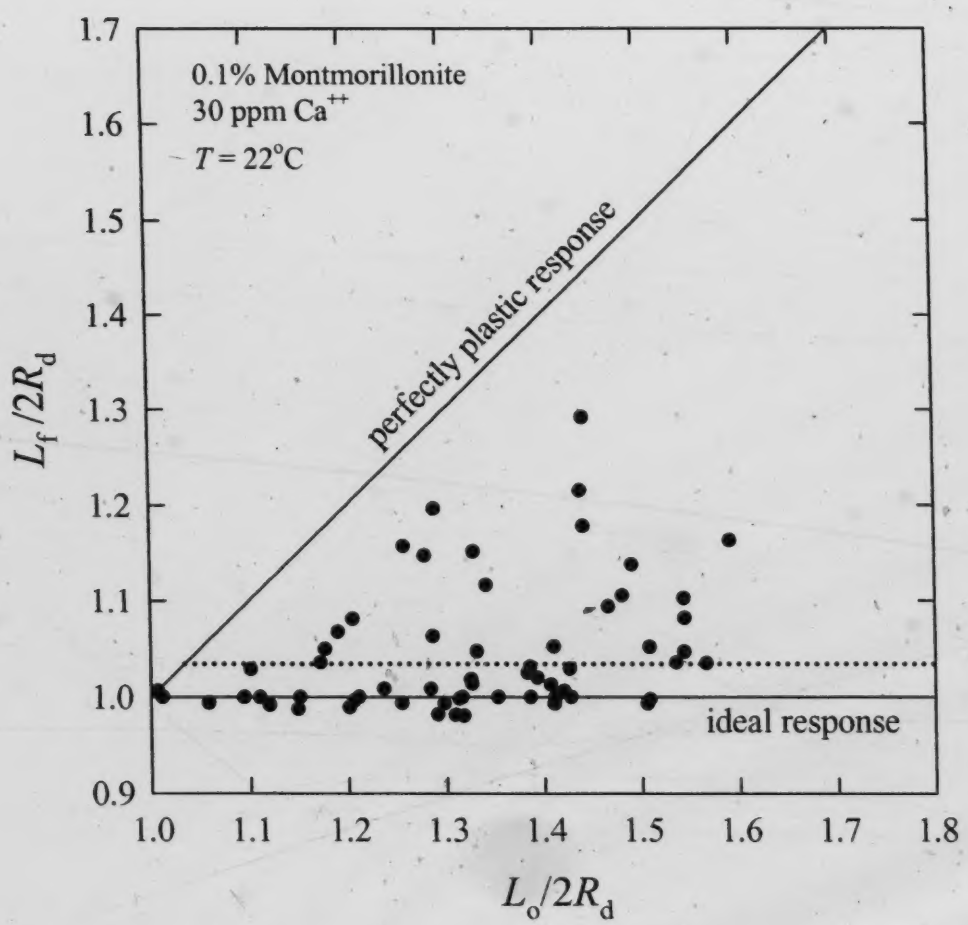

Figure 3.9: Static analysis of drop shape recovery experiments for bitumen drops in DIW+M+30ppm Ca^{++} at 22°C.

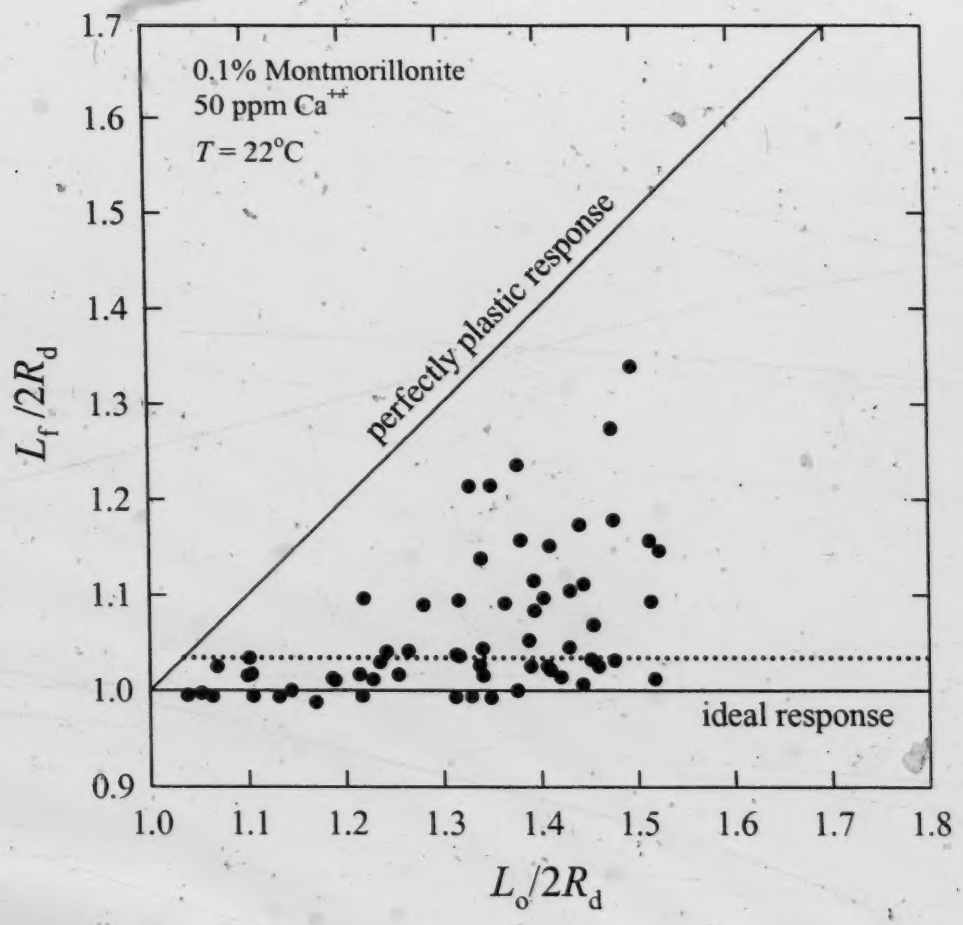

Figure 3.10: Static analysis of drop shape recovery experiments for bitumen drops in DIW+M+50ppm Ca^{++} at 22°C.

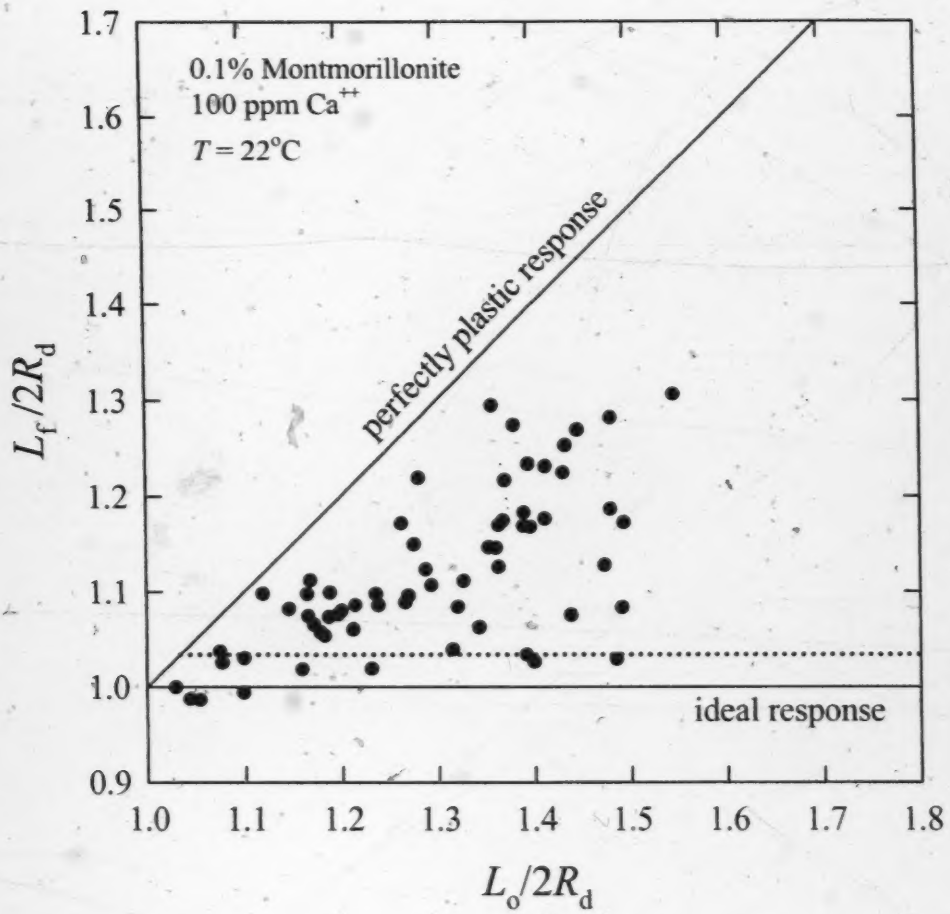

Figure 3.11: Static analysis of drop shape recovery experiments for bitumen drops in DIW+M+100ppm Ca^{++} at 22°C.

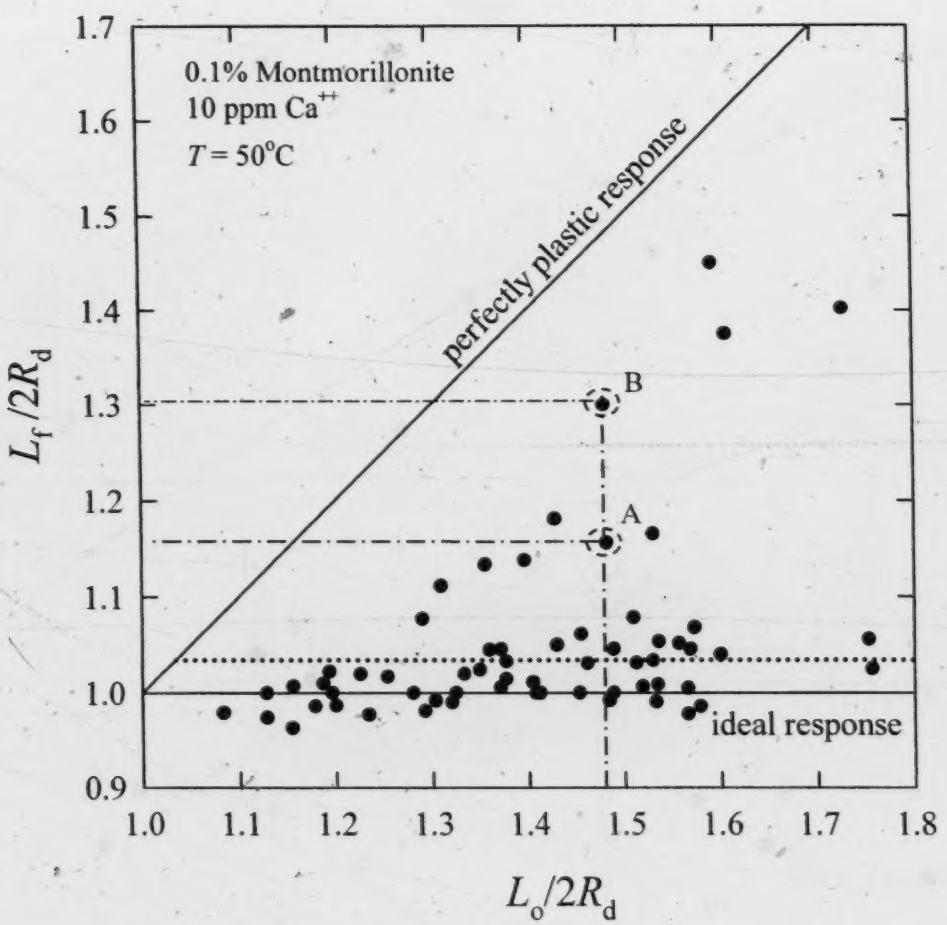

Figure 3.12: Static analysis of drop shape recovery experiments for bitumen drops in DIW+M+10ppm Ca^{++} at 50°C.

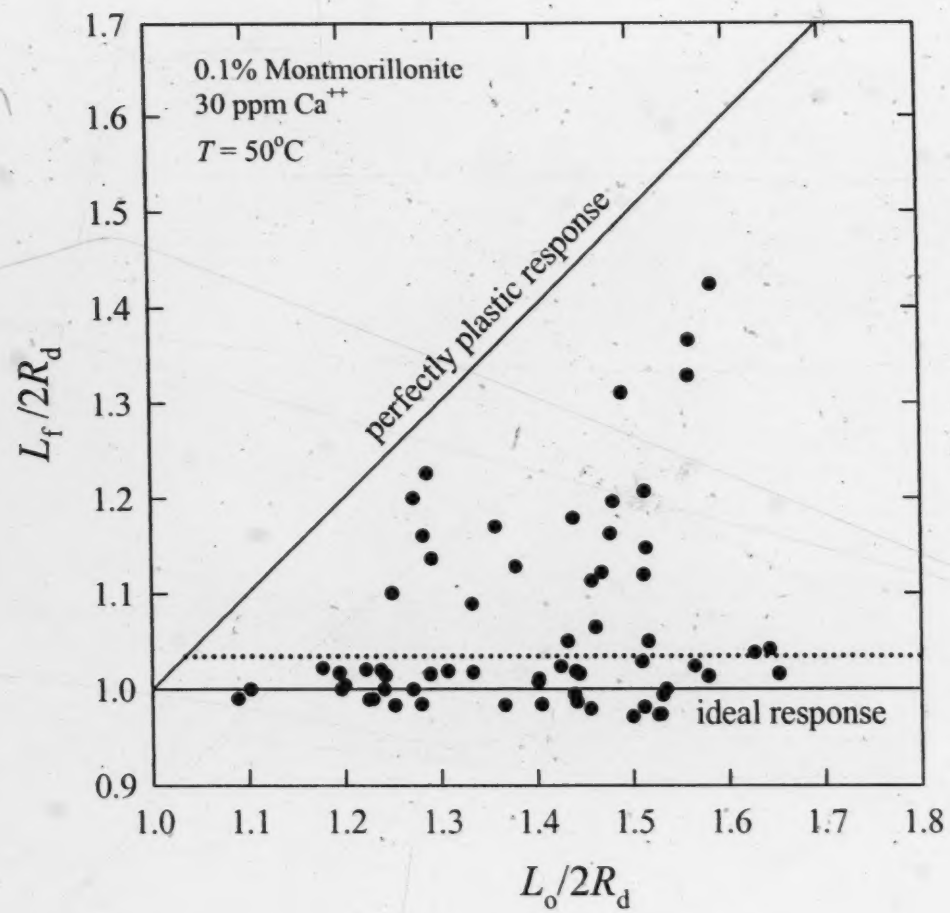

Figure 3.13: Static analysis of drop shape recovery experiments for bitumen drops in DIW+M+30ppm Ca^{++} at 50°C.

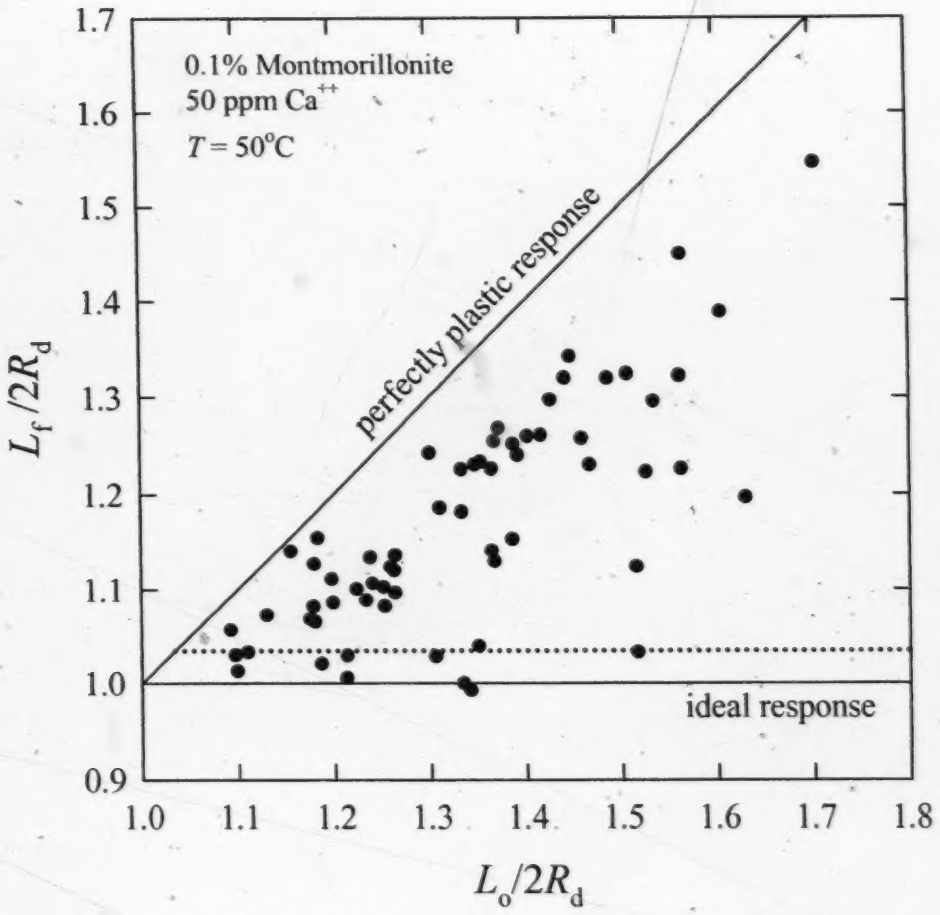

Figure 3.14: Static analysis of drop shape recovery experiments for bitumen drops in DIW+M+50ppm Ca^{++} at 50°C.

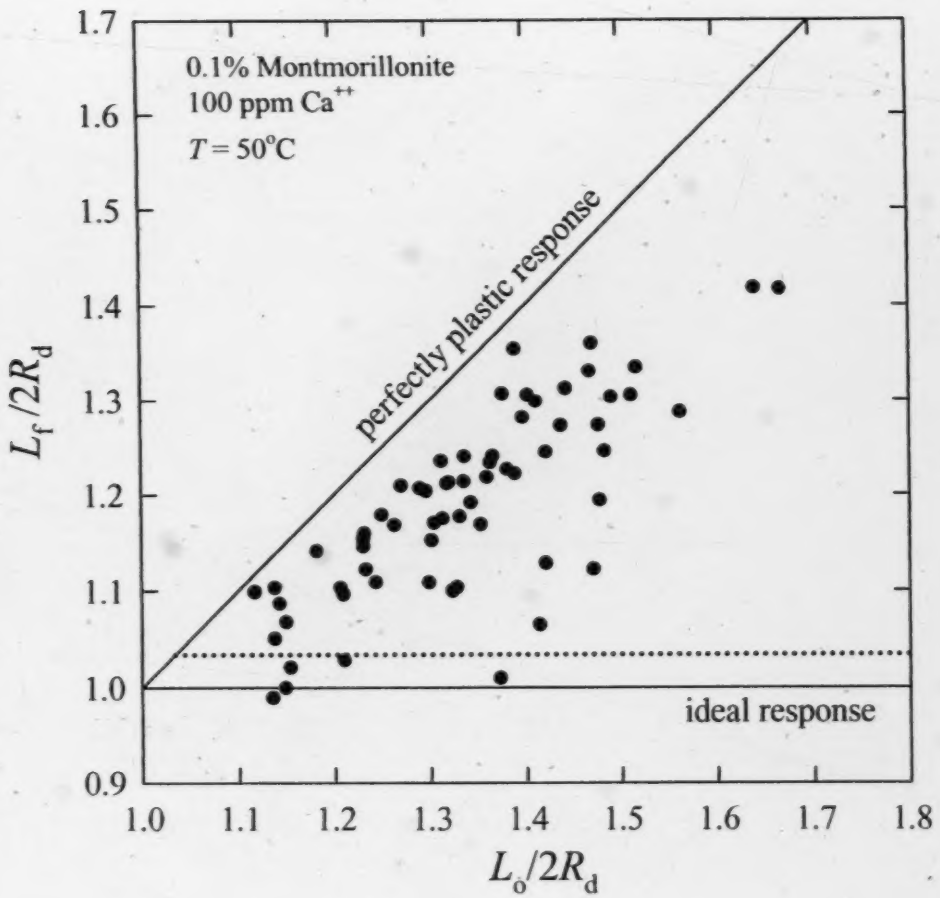

Figure 3.15: Static analysis of drop shape recovery experiments for bitumen drops in DIW+M+100ppm Ca^{++} at 50°C.

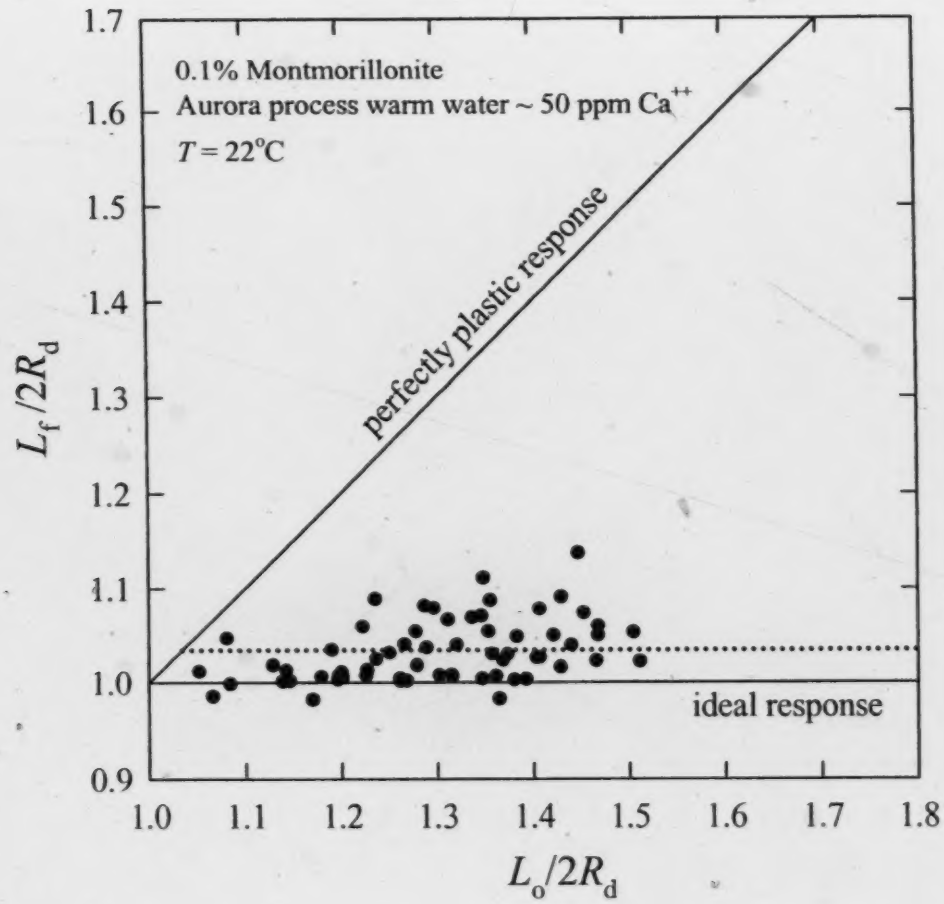

Figure 3.16: Static analysis of drop shape recovery experiments for bitumen drops in PW+M at 22°C.

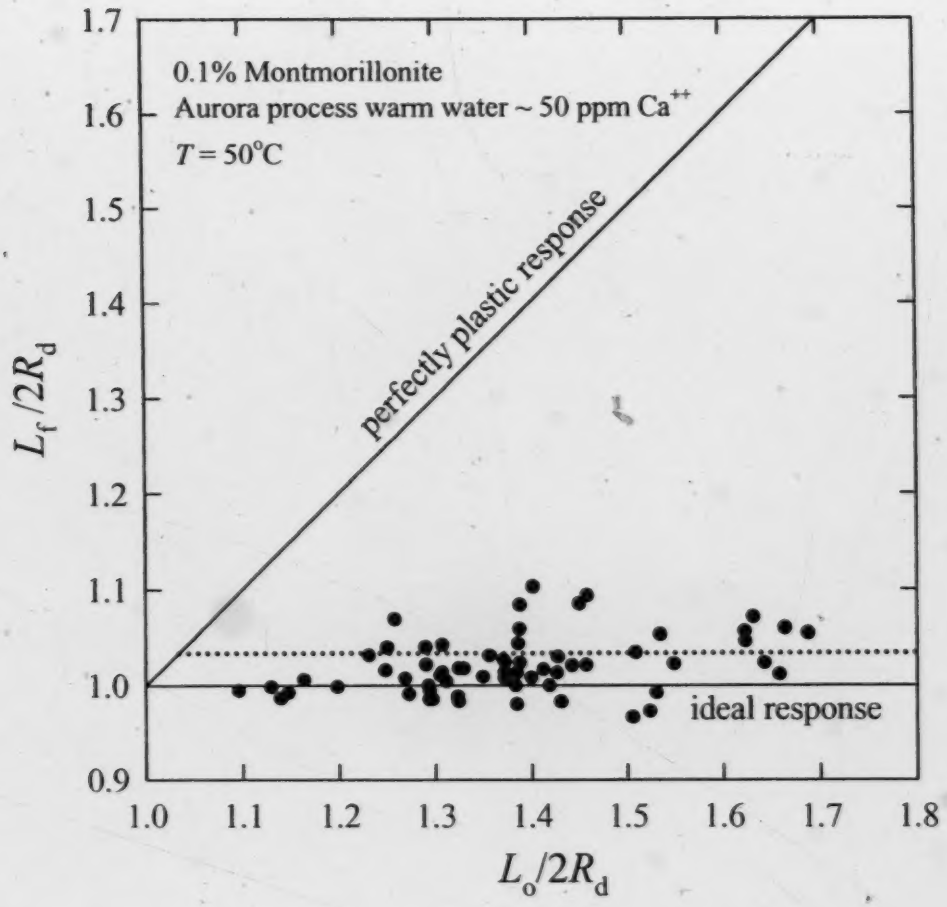

Figure 3.17: Static analysis of drop shape recovery experiments for bitumen drops in PW+M at 50°C.

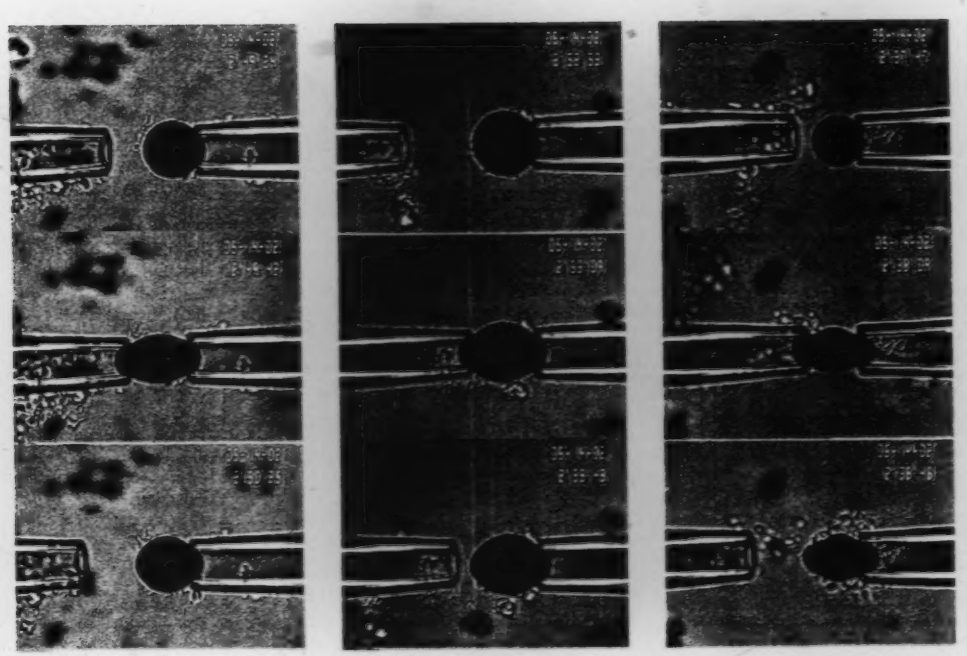

Figure 3.18: Sequential series of photographs (top to bottom) depicting a drop shape recovery experiment for a bitumen drop in DIW+M+50ppm Ca^{++} exhibiting (a) ideal behaviour, (b) plastic behaviour and (c) perfectly plastic behaviour. In drop shape recovery experiments, an initially spherical drop is axially stretched to a maximum deformation and released from one micropipette. The final photographs show the final drop shapes after the drops are allowed to equilibrate for sufficiently long time.

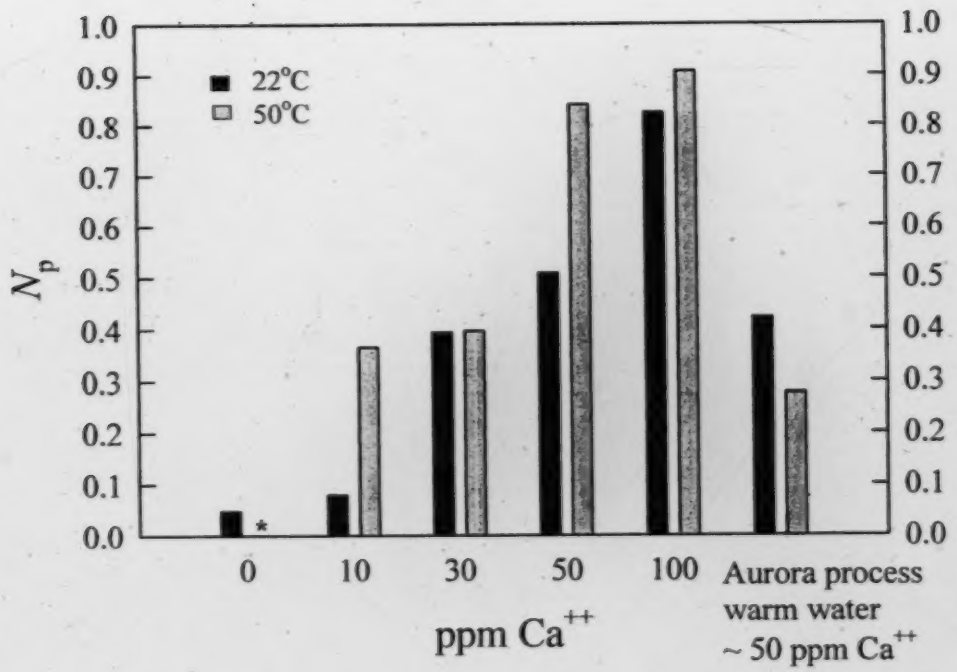

Figure 3.19: Effect of temperature and calcium ions on the fraction, N_p, of bitumen drops that behave plastically.

* The DIW+M system at 50°C was also observed. No signs of plasticity of bitumen drops surface were observed. However, no value is reported since bitumen drops quickly coalesced under the high temperature of 50°C. Thus, a smaller amount of bitumen drops was examined.

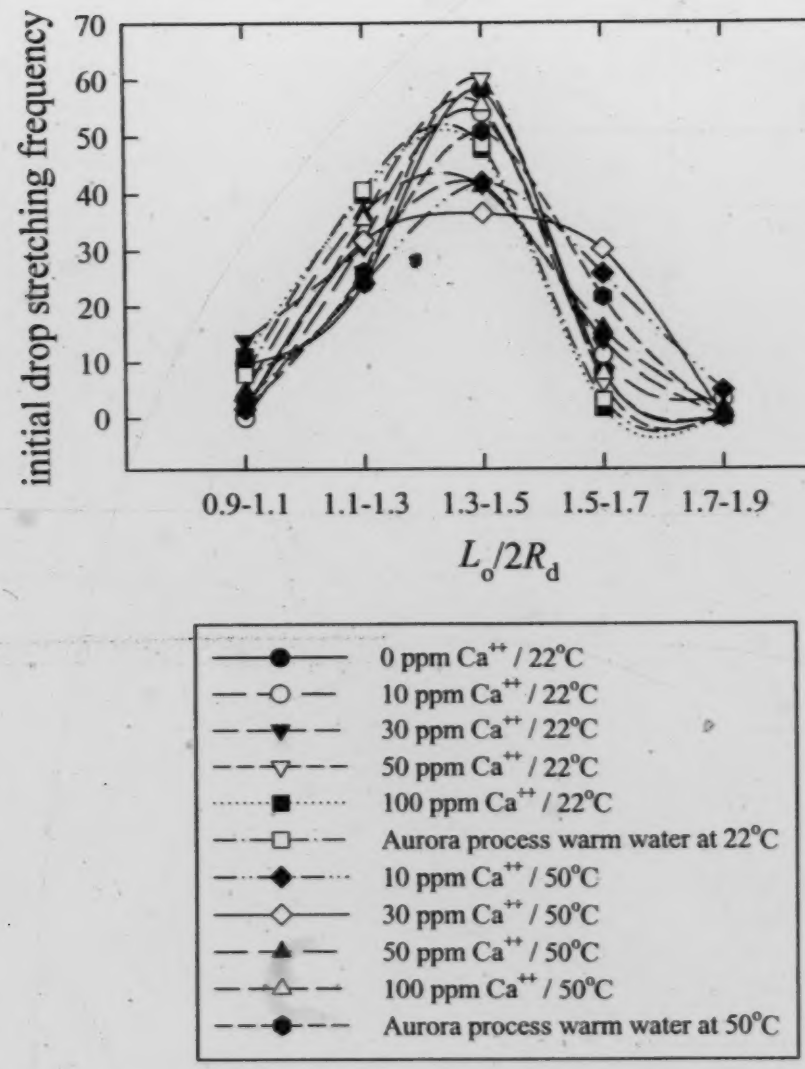

Figure 3.20: Frequency of initial stretching of bitumen drops based on the scaled maximum deformation to which drops are subjected when individually stretched between the micropipettes.

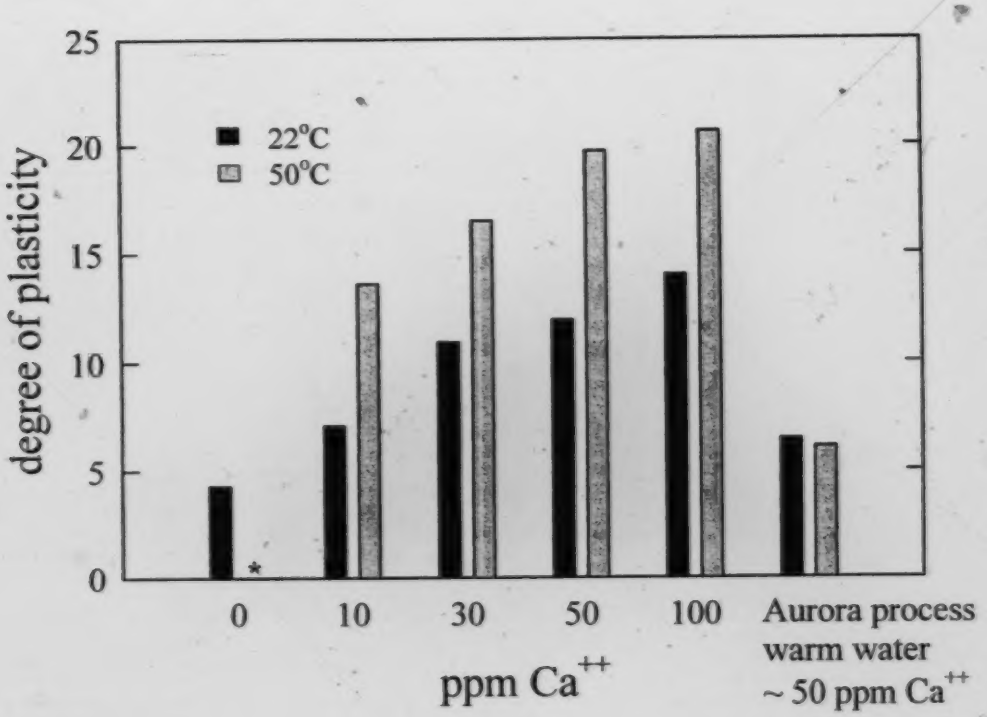

Figure 3.21: Effect of temperature and calcium ions on the degree of plasticity of bitumen drops.

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* The DIW+M system at 50°C was also observed. No signs of plasticity of bitumen drops surface were observed. However, no value is reported since bitumen drops quickly coalesced under the high temperature of 50°C. Thus, a smaller amount of bitumen drops was examined.

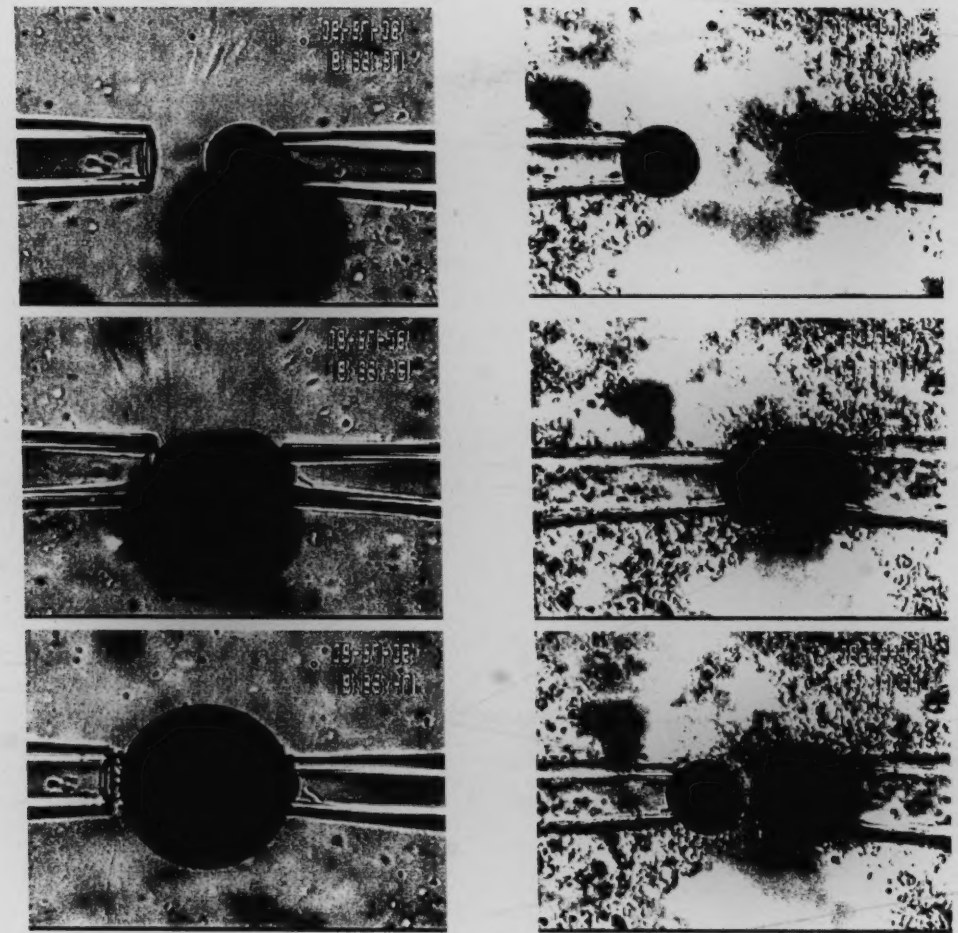

Figure 3.22: Demonstrating the stability of bitumen-in-water systems. Both experiments took place at 22°C. (a) Bitumen droplets coalesce upon contact in DIW+M system. (b) An attempt to induce coalescence by pressing two bitumen droplets together in DIW+M+100ppm Ca^{++} system. The droplets remained separate entities upon force withdrawal.

Chapter 4

4 Conclusions

4.1 Review of objectives

The micropipette technique was applied to directly explore the in-situ behaviour of single emulsion drops. Phenomena that are peculiar to the "smallness" of the emulsion drops (e.g. appropriate surface area-to-volume ratios, etc.) were accurately reflected in these unique experiments. All experiments were conducted under an inverted microscope. Two different emulsion systems that occur during oil sands processing were investigated. Thus, in chapter 2, water-in-diluted bitumen emulsions were examined and the objectives were to:

1. Test the rigidity of water droplets in diluted bitumen by varying the bitumen concentration and solvent ratio. A mixture of heptane and toluene (referred to as heptol) was used as solvent.
2. Measure the interfacial tension of the above systems.
3. Test interfacial rigidity as a function of pH using a solvent of toluene:heptane=1:1.

In chapter 3, bitumen-in-water emulsions were studied and the objective was to examine the surface behaviour of bitumen drops upon being individually stretched under various experimental conditions. More specifically, it was intended to:

1. Observe the drops' response in de-ionized water to which montmorillonite clays and/or calcium ions were added. The effect of increasing calcium ions concentration was further examined.
2. Demonstrate the effect of temperature in bitumen drop surface behaviour. Room temperature (22°C) and a higher temperature of 50°C were used as the operating temperatures. Examine bitumen droplets surfaces when emulsified

in Aurora process water (which consists of ~50ppm Ca^{++}) to which montmorillonite clays were added. In addition, the effect of temperature on the above system was also observed.

The conclusion obtained for each group of objectives will be discussed in the following sections.

4.2 Summarized results for water-in-diluted bitumen emulsions

Interfacial tension measurements and stability tests were conducted for water-in-diluted bitumen systems. Various bitumen concentrations and solvent compositions (i.e. toluene-heptane ratios) were used for emulsions preparation. In general, the interfacial tension on the water droplet surfaces decreased as bitumen concentration increased – i.e. more surfactants accumulated on the interface. In addition, there was little effect on the interfacial tension when using different solvent mixtures.

Furthermore, crumpling of the interface was influenced by bitumen concentration and type of solvent. For all solvents used, no crumpling was found for bitumen content less than 0.01%. This was probably due to the very low bitumen concentration in the bulk phase, and thus, surfactant concentration on the interface. Using de-ionized water (pH=5.4-5.6), crumpling was observed to occur at higher bitumen concentration. For heptol[100], crumpling disappeared at C_o>1% and at C_o>10% for heptol[30].

Finally, crumpling was strongly affected by the water pH. For the case of heptol[50], at higher pH, the crumpling region that normally occurred at C_o>0.01% disappeared. In general, pH has a very strong effect on crumpling.

4.3 Summarized results for bitumen-in-water emulsions

It has been concluded that the presence of both calcium ions and montmorillonite clays contributes to the plasticity of bitumen drops. Referring to DIW+M+Ca^{++} systems, increases in both temperature and calcium ion concentration result in a similar increase in the number and the degree of plastic bitumen drops.

In contrast, bitumen drops in PW+M systems exhibit no significant plasticity in their surfaces when containing considerable amounts of Ca^{++} ions and/or are elongated under higher experimental temperature.

The coalescence upon contact of bitumen droplets in water at 22°C was tested. It was observed that bitumen droplets coalesced upon contact in a DIW+M system. The addition of calcium ions to such a system may lead to the formation of CaM aggregates, which, in turn, creates an adsorbed film capable of preventing both coalescence and coagulation of bitumen droplets.

Chapter 5

5 Recommendations for future work

5.1 Recommendations for future work

In this study, both types of emulsions, water-in-diluted bitumen and bitumen-in-water, were studied. This work provided several answers regarding the conditions which affect emulsion behaviour. However, there are some thoughts for future work that will be outlined below.

Water-in-diluted bitumen emulsion rigidity was studied by deflating a water droplet via a micropipette. Surface material accumulates on the interface and creates a rigid interfacial layer. The adsorption of this material is probably well associated with the interfacial area available for adsorption. A larger amount of surface active species will probably adsorb on a larger water drop (and thus, a larger interfacial area available for adsorption). Furthermore, crumpling of the interface may appear at an earlier stage during water withdrawal via the micropipette when dealing with a larger (but always micron-size) water drop. Better control of the suction pressure applied at the micropipette tip will allow examination micron-size water drops of specified volume and thus, provide useful information regarding the adsorption mechanism. Therefore, it is important to adapt the micropipette apparatus in order to study the behaviour of volume-controlled emulsion drops.

In addition, comparisons between micron-scale and macro-scale (on order of millimetres) experiments would be very beneficial. It would be interesting to see if similar interfacial properties are observed for millimetre sized water droplets. In

other words, combining different length scale studies would be a big step forward in oil sands research.

It was concluded in chapter 2 that the composition of the diluent plays an important role on drop rigidity. In an attempt to improve the dewatering efficiency, it was discovered that paraffinic solvents at sufficiently high diluent-to-bitumen ratio result in a very clean and dry product (Czarnecki, 2001). Further investigation on emulsion rigidity via the micropipette technique, when dealing with different solvents, would gain deeper insights into the chemical composition and remarkable stability of the formed interfacial layer.

For the most part, industrial processes involving emulsions operate at temperatures and pressures different from "standard" conditions (i.e., one atmosphere and room temperature). As an example, pressurized flooding of largely depleted oil reservoirs (during which formation of crude oil-water emulsions is very common) may be involved in secondary and tertiary oil recovery techniques (Bond, 1974). In addition, although the oil sands industry is aiming at lowering operating temperature during extraction, many processes, such as froth dewatering, still operate at elevated temperatures of ~80°C (Czarnecki, 2001). Apart from the present ability to study the thermomechanical properties of emulsion drops (the microscope is equipped with a heated microscope stage), it is still important to adapt the apparatus for examining the pressure-dependent properties of emulsion drops. Generally, when referring to emulsion systems, the fulfilment of a wider range of coalescence experiments will provide additional information on the stability of such emulsions. Also, the possibility of time-dependent adsorption mechanism of the various species on the interface should be further investigated.

Specifically for bitumen-in-water systems examined in chapter 3, it has been mentioned that all shape recovery experiments took place by individually elongating bitumen drops up to a maximum length L_o. Here, the results of these

experiments are a first order approximation of the overall phenomenon of plasticity of bitumen drops when emulsified in aqueous environment. One further step would be to stretch a group of bitumen drops up to a specified scaled length $L_o/2R_d$ and then let them recover naturally. It would be beneficial to find ways to better control the drops maximum elongation. This will give additional insight regarding the plasticity phenomenon and will provide information for a higher order model.

Finally, crude oil is extracted from oil sands by mixing mined ore with process water, air and different chemicals. Here, "coker-feed" bitumen has been used. This bitumen has been "cleaned" by the removal of solids prior to downstream processing. Thus, the bitumen used in the present study is rather refined relative to the indigenous bitumen in the oil sands ore. Furthermore, a variety of water-soluble components, indigenous to bitumen, may be released into the process water, which is eventually used as an additional source of water (i.e. gets recycled back to the beginning of the extraction process). Many of these species are not reflected into the de-ionized water used in the major part of this study. In addition, many demulsifiers are added in commercial oil sands extraction. Thus, in order to better represent the emulsions found in oil sands extraction processes, it is imperative that material properties of bitumen drops obtained from oil sands ore be further examined in commercial process waters.

"Further research is needed to fully understand the physics of emulsion formation, particularly that of the rate of formation and the amount of energy required for formation. Models of emulsification are still at a crude state-of-the-art, however, the most await the data from new physical studies before they can be improved" (Fingas, 1995).

5.2 References

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Appendix A

Appendix A: Chemical composition of Aurora process warm water

Table A.1: Analytical chemical composition of Aurora process warm water.

Substance	ppm
Al 396.1	-0.008u
B 249.6	2.116
Ba 455.4	0.351
Ca 396.8	49.067
Cd 226.5	-0.087u
Co 238.8	-0.087u
Cr 267.7	-0.006u
Cu 327.4	0.004
Fe 238.2	-0.082u
K 766.5	13.500
Li 670.8	-0.071u
Mg 279.6	20.593
Mn 257.6	-0.120u
Mo 202.0	-0.018u
Na 589.6	559.12x
Ni 231.6	-0.092u
P 213.6	0.093

Table A.1: Analytical chemical composition of Aurora process warm water (continuing).

Pb 220.4	-0.092u
S 182.0	53.926
Sb 217.6	0.211
Se 196.0	0.014u
Si 251.6	6.009
Sn 189.9	Uncalc
Sr 407.8	0.742
Ti 337.9	-0.089u
V 311.8	-0.074u
Zn 213.9	-0.085u
Zr 343.8	-0.035u

Appendix B

Appendix B: Statistical analysis of stretched droplets distribution

Table B. 1: Statistical analysis of stretched droplets distribution using the ANOVA method.

Groups	Count	Sum	Average	Variance
0 ppm Ca^{++}/22°C	8	62	7.75	47
10 ppm Ca^{++}/22°C	8	63	7.875	47
30 ppm Ca^{++}/22°C	8	65	8.125	29
50 ppm Ca^{++}/22°C	8	65	8.125	61
100 ppm Ca^{++}/22°C	8	63	7.875	46
Aurora sample /22°C	8	64	8	56
10 ppm Ca^{++}/50°C	8	62	7.75	29
30 ppm Ca^{++}/50°C	8	63	7.875	52
50 ppm Ca^{++}/50°C	8	63	7.875	33
100 ppm Ca^{++}/50°C	8	65	8.125	63
Aurora sample/50°C	8	65	8.125	49

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	1.818	10	0.181	0.003	1	2.56
Within Groups	3618	77	46.9			
Total	3619.81	87				